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Direct graphene growth on Si surface with high power pulsed plasma

Yuto Oishi[1], Akihiro Iwata[2], Masanori Shiohara[2], Takashi Matsumoto[3]
[1] Graduate school of Engineering, Fukuoka Univ.,
[2] Department of Electrical Engineering, Fukuoka University
[3] Tokyo Electron Technology Solutions Limited
e-mail: sinohara@fukuoka-u.ac.jp

Graphene is one of promising materials for future devices, because graphene has a lot of useful properties, such as low resistivity, high current density resistance and so on [1]. Wiring on Si devices is one of the most important applications. To use the wiring for Si devices, graphene should be grown over large area on a Si surface at low temperatures, at least below 600 ℃. Graphene is often grown at high temperatures. And also, catalysis should not be used when graphene is deposited. Metals, like Cu and Ni, are frequently used as catalysts for graphene growth. These metals are the potential contaminants of silicon, which degrades the device characteristics.

Some studies revealed graphene could be grown without catalysis at low temperatures by using plasma processing, especially, by using microwave plasma, suggesting that high density plasma is required for the graphene growth at low temperatures [2]. Then, we adopted high power pulsed sputtering (HPPS) plasma, which is recently attracting for sputtering deposition of various materials, because the plasma generates high energy electrons and high electron density by pulse power. HPPS plasma could also effectively generates high-energy species in its plasma. To generate high-energy chemical species, a hybrid method of a sputtering with a plasma-enhanced chemical vapor deposition (PECVD) method has been developed. A circular carbon target with a diameter of 70-mm was used for sputtering, and styrene (C_8H_8) was used as a source molecule for PECVD. This is because the sputtering rate of carbon target is low. Styrene was added into the deposition process to supply effectively carbon related species.

Unbalanced magnetic field was emitted from the target by placing one magnet in the center of the backside of the target, and eight magnets surrounding the center. The unbalanced magnetic field was designed to enable the plasma to reach the substrate, which was set 150 mm apart from the carbon target.

The silicon substrate was used for the graphene deposition. The size of the substrate was 5 mm × 20 mm, with a thickness of 0.5 mm. The substrate was positioned in the floating condition. The substrate was heated with resistive heating. The substrate temperature, controlled with the direct current, was monitored with a pyrometer.

Target current, which determines all plasma current, was controlled with the protective resistance connected in series to the carbon target from the direct power supply. The magnitude of the protective resistance was controlled by combining a few 10 Ω resistors to make 10, 15 and 30Ω.

Before every experiment was performed, the chamber was evacuated under 10^{-4} Pa using vacuum system with a turbo molecular pump and a rotary pump. Before the plasma generation, styrene of 0.75 sccm was introduced into the chamber, and hydrogen gas of 15 sccm was also introduced into the chamber via a mass controller. The flow rate of the styrene was determined by controlling the chamber pressure. After the chamber pressure was set at 1.3 Pa, pulsed plasma was generated by giving pulsed high direct voltage of ―850 V with 1% duty of 500 Hz to the carbon target.

In this study, the magnitude of the target current was optimized by the protective resistance. When 30, 15 and 10 Ω resistance was connected to the target as protective resistance, maximum target current during plasma was 20, 40 and 59A, resistively. The substrate temperature was set at 800 ℃. The growth time was set at 5 min. The grown films were measured with Raman spectroscopy. Each Raman spectrum has D, G, D', and 2D peaks, indicating that the structures of the grown films were formed by six-membered rings, like carbon nanowall, and graphene.

SEM observation of the surface morphology revealed flake-like structures were formed when the target current is set at 59A; It was suggested that carbon nanowall structure were formed. On the other hand, the flat surfaces were observed under the target currents of 20 and 40A. These results suggest that high currents increased ion density and ion impact on the substrate. As a result, carbon nanowalls might be grown. To suppress the growth of theses carbon nanowalls, target current, this is, ion density and ion impact on the substrate, should be suppressed.

TEM images of the grown films were also acquired. These images show the layered structures were observed when the target current is set at 20 and 40A. These results indicate graphene might be formed when the target current was limited.

From the analysis of Ramana spectra of the films, I(D)/I(G) was 4.54 and 1.76, when the current was set at 20, and 40A, respectively. It is suggested that the density of vacancies increased, when the target current decreased from 40A to 10A. The decrease of the target current deteriorates the graphene crystallinity.

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