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Synthesis of Graphene by Plasma Process
グラフェンのプラズマプロセス合成

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Graphene with high electrical conductivity has been synthesized by using hydrogen plasma treatment of copper foils for 30 seconds at the temperature of 850 ℃ together with joule-heating treatment of the foils without using a carbon-containing gas such as methane in order to suppress the nucleation density of graphene. The domain size of synthesized graphene, the controllability of a few layers and the electrical conductivity have been significantly improved compared with plasma chemical vapor deposition (CVD) using carbon-containing gas. The sheet resistance of bilayer graphene exhibits 951 Ω in average. The carrier mobility shows 1000 cm^2/Vs in maximum at room temperature. The sheet resistance of 130±26 Ω has been attained after the doping by gold chloride solution.

1. Introduction

For the mass production of graphene by such as roll-to-roll method the problem of thermal CVD is the thermal load on the apparatus given by the process temperature of higher than 1000 °C. It is also required a significant reduction of synthesis time. An attempt has been made to reduce the thermal load on the apparatus by direct joule heating of copper foil substrate and to demonstrate the roll-to-roll synthesis of graphene at 950 °C. [1] While good properties (sheet resistance of 200 Ω and the transmittance of 97.1 %) have been reported, much higher throughput and lower synthesis temperature have been expected to lower the cost and to improve the quality of graphene films. We have attempted to develop a plasma-enhanced CVD of graphene to lower the synthesis temperature and the process time at the same time. [2][3] Current problem of the plasma CVD of graphene is the crystal size of 10 nm or smaller, which inhibits the electrical conductivity. In this study, we attempt to expand the size of the graphene crystal and to improve the controllability of a few layers by reducing the concentration of the carbon source used for graphene synthesis which is expected to suppress the nucleation density.

2. Experimental

Tough-pitch copper foils of 6.3 μm-thick were used for substrate of graphene synthesis. We synthesize graphene on the condition of extremely low-concentration carbon source, which is supplied from copper foil substrate and/or environments in the reaction chamber by microwave plasma CVD apparatus, in particular, using hydrogen plasma treatment. Hydrogen plasma treatment is performed in 30 sccm flow and 5 Pa for 30 seconds using a surface wave plasma excited by 2.45GHz microwave.

3. Results and Discussion

We show a Raman spectrum for only hydrogen plasma treatment for 30 seconds without heat treatment of copper foil in Fig. 1(a).[4] In this case, no peaks attributed to carbon related materials such as graphene and amorphous carbon were observed. Figure 1(c) shows a Raman spectrum from copper foil subjected to hydrogen plasma treatment for 30 seconds subsequent to the treatment by the joule heating at 1000 ℃. Although very weak intensities of G-band (1580 cm^{-1}) and D-band (1350 cm^{-1}) were observed, 2D-band in the range of 2641 cm^{-1} to 2681 cm^{-1} was not observed, which indicates that graphene was not formed by at this temperature because of an extremely small amount of carbon supply accompanying with evaporation of copper substrate. Figure 1(b) shows a Raman spectrum from copper foil subjected to hydrogen plasma treatment for 30 seconds at 850 ℃ subsequent to the treatment by the joule heating at 850 ℃.

Distinct G-band and 2D-band are observed with a very low intensity of D band which indicates low defect.

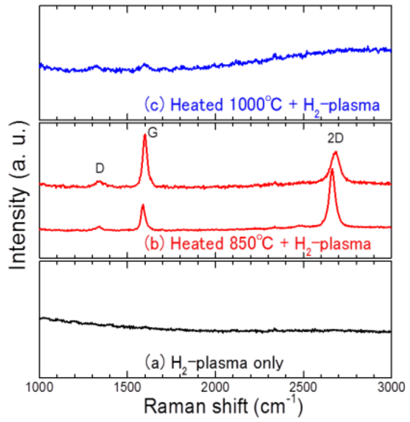

Fig. 1. Raman spectrum of copper foil at room temperature after hydrogen plasma treatment at each temperature. (a) Only hydrogen plasma treatment, (b) Hydrogen plasma treatment while heating 850 ℃, and (c) Hydrogen plasma treatment while heating 1000 ℃.

The sheet resistance of bilayer graphene exhibits 951 Ω in average. The carrier mobility shows 1000 cm^2/Vs in maximum at room temperature.[5] Figure 2 shows the sheet resistance map of the synthesized bilayer graphene film, which doped by gold chloride.[4] As shown in this figure, the sheet resistance of the average in 6 × 6 mm^2 was 130 Ω and the lowest sheet resistance was less than 100 Ω.

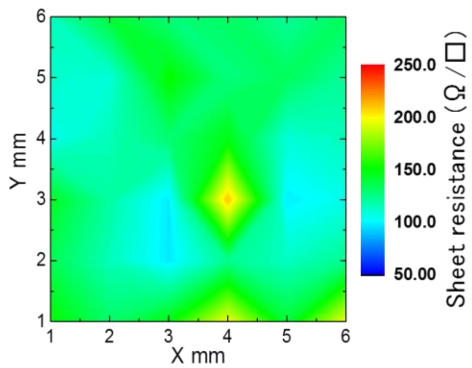

Fig. 2. Sheet resistance map of graphene film after wet doping by gold chloride.

4. Summary

Graphene with high electrical conductivity has been synthesized by using hydrogen plasma treatment of copper foils for 30 seconds at the temperature of 850 ℃ together with joule-heating treatment of the foils without using a carbon-containing gas such as methane in order to suppress the nucleation density of graphene. The domain size of synthesized graphene, the controllability of a few layers and the electrical conductivity have been significantly improved compared with plasma chemical vapor deposition (CVD) using carbon-containing gas. The sheet resistance of bilayer graphene exhibits 951 Ω in average. The carrier mobility shows 1000 cm^2/Vs in maximum at room temperature. The sheet resistance of 130±26 Ω has been attained after the doping by gold chloride solution.

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