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Electrical properties and domain sizes of graphene films synthesized by microwave plasma treatment under a low carbon concentration

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ABSTRACT

We performed Hall effect measurements and Raman mapping of graphene synthesized by microwave plasma treatment under a low carbon concentration. The Hall mobility and average domain size were estimated to be 100–1000 cm^2/Vs and around 30–100 nm, respectively, which are much higher than those of graphene deposited by conventional plasma chemical vapor deposition. In addition, dark-field transmission electron microscopy images showed domain sizes of around 100 nm. Thus, this method is expected to easily produce a large amount of high-quality graphene with high throughput.

1. Introduction

Graphene [1–5] is a potential future electronic material with high mobility, high thermal conductivity, high optical transparency, and flexibility. For example, graphene transparent conductive films are required for flexible electronics such as touch panels [6–8], organic light-emitting diodes [9–11], and organic photovoltaics [12–13], which cannot be realized with conventional materials such as indium tin oxide. To develop applications of graphene films, it is important to realize their mass production. Chemical vapor deposition (CVD) [14–16] is one of the most suitable techniques for producing graphene films with large sizes. Recent study has shown that thermal CVD combined with a roll-to-roll synthesis technique can continually produce graphene films [17]. Furthermore, we have developed a microwave plasma CVD technique combined with the roll-to-roll process [18] that has realized fast synthesis of graphene films at low temperature in a few tens of seconds. When graphene is produced by plasma CVD at low temperature, on the other hand, its Hall mobility and average domain size are limited to 10–100 cm^2/Vs and around 10 nm, respectively [19]. Smaller domain sizes of graphene could degrade its electrical properties, so ensuring a larger domain size is essential for improving the electrical conductivity of graphene films. Decreasing the carbon concentration during the graphene synthesis is one way to accomplish this [20]. Plasma exposure enhances the decomposition of the gas and activation by the catalyst, resulting in a high growth rate of the graphene. If the carbon concentration is high, the nucleation density on the metal catalyst

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is increased, resulting in a smaller domain size. For plasma CVD, the carbon concentration must be much lower than that for thermal CVD.

In this study, we report the electrical properties and crystallization of the graphene films synthesized by plasma treatment under a low carbon concentration as determined by Hall effect measurements and Raman mapping, respectively. We demonstrate a graphene synthesis without CH_4 gas, in which the carbon source could be the carbon-containing catalytic metal and/or the inside of the CVD chamber. In addition, we estimate the domain size directly from dark-field transmission electron microscopy images. As demonstrated by these results, this method is expected to easily produce a large amount of high-quality graphene with high throughput.

2. Experimental

Fig. 1 shows a schematic illustration of the microwave plasma treatment equipment. The waveguide is equipped with a slot antenna that emits microwaves at 2.45 GHz through a quartz window into the chamber. High-density surface-wave plasma is excited along the surface on the quartz window (surface heating mode), which effectively suppresses the unintentional heating and ion bombardment of the metal substrate. In this experiment, catalytic copper (Cu) foil was suspended in the chamber, where it was heated by Joule heating when current was flowed through it. Such use of Joule heating is useful for suppressing electricity consumption. A two-step process was used to synthesize the graphene films by plasma treatment. First, the surface of the copper foil was cleaned by increasing the temperature. Then, the graphene synthesis was performed with only H_2 plasma exposure. The lower carbon concentration could suppress the nucleation density, resulting in a higher quality of the graphene films. The carbon source could be the carbon-containing Cu foil and/or the inside of the chamber. The carbon concentration in copper foil is estimated to be about 10 ppm by combustion method, and the out gas from the chamber is measured to be about 1.5×10^{-4} Pa/s. The substrate temperature during graphene synthesis is estimated to be about 800–1000 °C, as calculated from the measured resistance of the Cu foil. The synthesis pressure was 5–10 Pa, and the synthesis time was around 30–90 s.

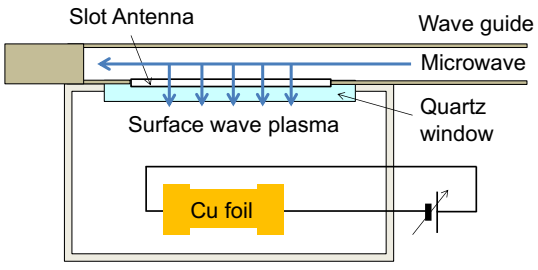

Fig. 1 – Schematic illustration of the plasma procedure equipment. The Cu foil is connected to an external voltage supplier. (A color version of this figure can be viewed online.)

The fabrication of the van der Pauw device proceeded as follows. First, the graphene film synthesized by microwave plasma treatment was coated with poly(methyl methacrylate) (PMMA) layers, and the copper foil was etched with ammonium persulfate aqueous solution. Then, the graphene film was transferred onto quartz substrates. After the transfer process, van der Pauw devices for the Hall effect measurements and Raman mapping were fabricated using conventional photolithography, metal deposition, and lift-off processes. O_2 plasma was used to pattern the graphene film, and the metal electrode (Au/Ti = 200/50 nm) was deposited on the patterned graphene. To confirm the device structure, it was measured by scanning electron microscopy (SEM) in which the acceleration voltage was 1.0 kV.

Laser light with a wavelength of 532 nm was used for the Raman measurements. A Hall effect measurement with an AC magnetic field (B = 0.35 T) was carried out on the van der Pauw devices under an air atmosphere. Carrier density (n) is estimated by $n = BI_s/eV_{Hall}$, and Hall mobility (μ_{Hall}) is estimated by $\mu_{Hall} = V_{Hall}/BR_sI_s$ (I_s is current applied to the sample, e is elementary charge, V_{Hall} is Hall voltage, R_s is sheet resistance). To measure the electrical properties of the devices, a gold wire was connected between the device electrode and the sample holder.

In addition, the powerful dark-field transmission electron microscopy (TEM) technique was used to confirm the domain size of the graphene films directly [21]. The sample was prepared as follows. Graphene films synthesized by plasma treatment were transferred to a Mo Quantifoil grid using PMMA. The sample was subsequently annealed in air at 200 °C for 10 min and inserted into the TEM equipment. The acceleration voltage of the HR-TEM was 120 kV.

3. Results

Fig. 2(a) shows a SEM image of the fabricated van der Pauw device. Graphene films with areas of $90 \times 90\ \mu m^2$ were confirmed to connect to each electrode. The average layer number of the graphene films in this study is estimated to be about two from the optical transmittance measurements, under the assumption of 2.3% absorption per layer [22]. Fig. 2(b) shows a typical single Raman spectrum for the graphene film in a fabricated device. A 2D-band peak due to a second-order process and a G-band peak due to the doubly degenerate zone center mode are obtained in Raman spectra at ~2700 and ~1600 cm^{-1}, respectively. This indicates that graphene films were indeed obtained. In addition, a small D-band peak (disordered graphite) is detected at ~1355 cm^{-1}, indicating a high quality of the graphene films. The peak intensity ratio between the D and G bands (I_D/I_G) is a convenient index for estimating the domain size of the graphene [23–24] which is estimated by following equation: D_{GR} (nm) = $(2.4 \times 10^{-10})\ \lambda^4\ (I_D/I_G)^{-1}$ (λ is laser wave length using Raman measurement). It is estimated as about 100 nm for the graphene synthesized in this study.

We performed Raman mapping to quantify the defects and/or disorder of the graphene films and measured the Hall mobility to evaluate the electrical conductivity. Fig. 3 shows the Raman peak intensity ratio (I_D/I_G) maps in areas of