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Large area coating of graphene at low temperature using a roll-to-roll microwave plasma chemical vapor deposition

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ABSTRACT

Roll-to-roll microwave plasma chemical vapor deposition (CVD) at low temperature has been developed for the fabrication of a continuous and large area deposition of graphene films for the application of transparent conductive films. Deposition of graphene films on copper (Cu) foils, under methane (CH_4) and hydrogen (H_2) plasma below 380 °C, were confirmed and characterized by Raman spectroscopy. In addition, the film qualities were improved by controlling the $CH_4/(CH_4+H_2)$ ratio and the process pressure. The graphene film obtained by roll-to-roll microwave plasma CVD process exhibited uniform Raman spectra towards the width direction of the Cu foil (A4 width). Transmittance and haze of the films were confirmed to be uniform and are in sufficient quality for the use of practical touch panel applications.

1. Introduction

Transparent conductive films are essential components for many modern electronic and optoelectronic applications such as displays, touch screens, solar cells and light emitting devices. Although the commercial transparent conductive films used for practical applications are made from indium tin oxide (In_2O_3:Sn, ITO), a substitute material for ITO has been a topic of great interest, due to the limited supply of indium and other rare-metals. In addition, recent advance in organic semiconductor have realized flexible electro-optics devices such as electronic papers and sheet-type solar cells, for which inflexible ITO films are not applicable. Therefore, development of an alternative transparent conductive film has attracted much attention.

Graphene, which consists of only carbon (C) atoms, is expected to be one of the most appropriate materials for transparent conductive films, since an ideal mono-layer graphene has a transmittance of 97.7%, an electron mobility of 200,000 cm^2/Vs at room temperature and a thermal conductivity of 5000 W/mK. However, the development of graphene mass production technology has not been established up to now, since it requires either high temperature or long process time. Techniques such as thermal chemical vapor deposition (CVD) on metal catalysis require high temperature (about 1000 °C) and long process time (few tens of minutes) to form graphene films [1]. As for low temperature formation of graphene film, reduction process of graphene oxide was reported [2]. Although this process enables us to form large area graphene on various substrates using spin coating technique, damages and defects during oxidization process still remain in the formed graphene films. Using surface wave plasma CVD, high quality graphene films were obtained at low temperature and few tens of seconds [3]. In addition, touch panel application based on surface wave plasma CVD graphene was demonstrated [3]. From the previous reports, it is expected that the graphene deposition process using surface wave plasma CVD is suitable for an industrial mass production.

Roll-to-roll process is another common technique for industrial mass productions of large-area thin film. By combining roll-to-roll process and CVD technique, a continuous deposition process of graphene film is expected. Among various CVD methods, surface wave plasma CVD is selected for combination with roll-to-roll process, because of its possible low-temperature deposition of graphene.

In this paper, we describe the development of roll-to-roll microwave plasma (MWP) CVD process towards the industrial mass production of graphene films. In our previous report [3], Ar was used as the carrier gas to keep the plasma stable. However, Ar was considered to damage the graphene and incorporates unintentional impurities from the CVD system. Therefore, effects of flow ratio of CH_4 to the total gas (CH_4+H_2) and process pressure during CVD process on graphene qualities were examined in this study. A continuous graphene film with 294 mm width is deposited on copper (Cu) foils at low temperature of around 380 °C. High uniformity of transparency (95%) in large area is confirmed. Our data indicated that the roll-to-roll MWPCVD was a promising technique for the graphene mass production towards the transparent conductive films.

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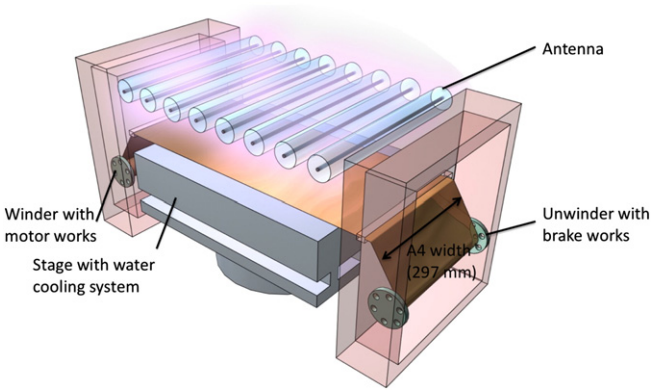

Fig. 1. The schematic of a roll-to-roll microwave plasma CVD apparatus based on a linear antenna type.

2. Experimental details

2.1. A roll-to-roll system in a linear antenna type microwave plasma CVD for graphene deposition

A MWPCVD process based on a linear antenna type system has been one of the potential technique for graphene deposition over large area at low process temperature, because MWP sustained by surface wave mode generates high plasma density (10^{11}–10^{12} cm^{-3}) even at relatively low pressure (<100 Pa), which is effective to keep the substrate at low temperature. Large area coating of nano-structured diamond films was established using such CVD processes [4,5].

Our linear antenna type MWPCVD system (Fig. 1) had eight coaxial linear antennas covered with quartz tubes, which were used to generate the plasma. The antennas were cooled by air in quartz tubes. The CVD apparatus was equipped with two microwave generators of 2.45 GHz with a maximum power of 20 kW. Source gases (methane: CH_4 and hydrogen: H_2) were introduced from the top of CVD chamber and evacuated from the bottom of the chamber using a rotary pump [6].

The roll-to-roll system consists of a pair of winder and unwinder. The winder has a motor attached in order to control the flow speed of metal foils in the range from 1 to 500 mm/s. The unwinder is equipped with a brake works to keep the appropriate tension of the metal foils. The sample holder is cooled by water supply. The metal foils are exposed to plasma during traveling of 48 cm length of plasma area. The numbers of deposited graphene layers can be controlled by foil transfer speed. A rolled 33 μm-thick Cu foils with 294 mm in width, prepared by rolling processes, are used as the substrates in this study. A metal foil of up to 30 m in length and 33 μm in thickness could be installed in our unwinder section [7].

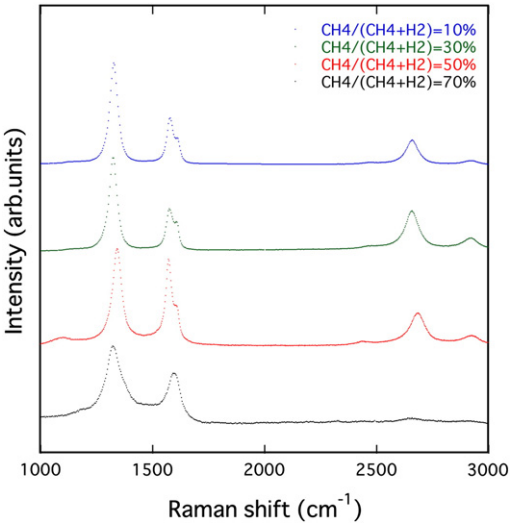

Fig. 2. Raman spectra of the obtained films, where the $CH_4/(CH_4+H_2)$ ratios were 10, 30, 50 and 70%.

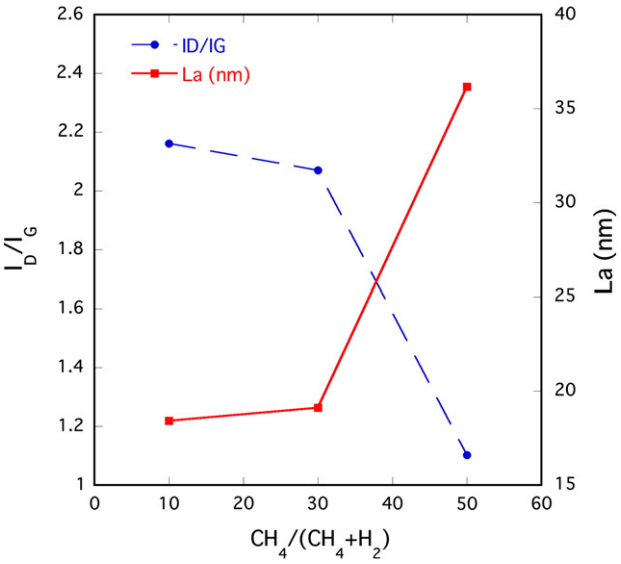

Fig. 3. The peak intensity ratio as a function of the $CH_4/(CH_4+H_2)$ ratio.

The typical CVD conditions in order to form continuous films were as follows. The microwave power was 12 kW. The temperature of sample stage was less than 380 °C. The flow ratio of CH_4 to the total gas (CH_4+H_2) [$CH_4/(CH_4+H_2)$] and the process pressure was controlled as parameters in order to obtain large domain size. The $CH_4/(CH_4+H_2)$ ratios were changed from 10 to 70%. In order to keep plasma stably, Ar was used during CVD process in our previous report [7]. However, Ar was not added in this study since Ar was considered to make damage on graphene and to make unintentional impurities from CVD and roll-to-roll system. The pressures in our CVD system were controlled from 30 to 300 Pa. The Cu foil follow speed was 5 mm/s, which let the Cu foil exposed to plasma for 96 s.

2.2. Characterization techniques of graphene films

The obtained graphene films on Cu foils were characterized by Raman spectroscopy excited by a 638 nm diode laser with a beam spot size of 1 μm in diameter.

Plane view transmission electron microscopy (TEM) observations were also carried out. Graphene films were mounted on Cu mesh grid. The accelerated voltage was 200 kV. Cross-sectional transmission electron microscopy (XTEM) observations were performed to estimate the length of graphene and the number of layers. In order to prevent unnecessary damage of graphene film prior to the XTEM observation, amorphous carbon was deposited on top of the graphene/Cu substrate. Gallium (Ga) focus ion beam (FIB) etching technique was used for sample preparations. For observations, accelerated voltage was 300 keV and the resolution of TEM used in this study was about 2 nm.

In order to evaluate a transmittance, haze and sheet resistance of the film, the substrates (Cu foils) were removed by dipping the sample into a solution of ferric chloride ($FeCl_3$) and the graphene films were transferred onto PET films. The transmittance and the haze at 550 nm were measured by means of visible light spectroscopy. The illuminated area was about 0.7 mm in diameter. Four-probe method was used to measure the sheet resistance. The distance between probes was 1 mm. The measurements were carried out in air at room temperature.