Low Temperature Growth of Carbon Nanomaterials on the Polymer Substrates by Microwave Plasma Technique

R.V. Bekarevich1,2, S. Miura1, A. Ogino1, A.U. Rahachou2 and M. Nagatsu1
1Graduate School of Science and Technology, Shizuoka University, 3-5-1 Johoku, Naka-ku, Hamamatsu 432-8561, Japan
Fax: +81-53-478-1081, e-mail: tmnagat@ipc.shizuoka.ac.jp
2Francisk Skarina Homel State University, Sovetskaya 104, Homel 246019, Belarus
Fax: +375-232-57-82-53, e-mail: rbekarevich@yandex.ru

In this study, multi-walled carbon nanotubes and few-layer graphene sheets have successfully grown on Si and polyimide substrates at relatively low temperature of 230~260°C by the microwave-excited surface wave plasma technique. Graphite-encapsulated Ni nanoparticles have been used as the catalyst for growing CNMs in NH3/CH4 plasma. It has been found that bias voltage and nature of the substrate can greatly influence the CNMs structure.

Key words: multiwalled carbon nanotubes, few-layer graphene, high resolution TEM, microwave-excited surface-wave plasma CVD

1. INTRODUCTION
Carbon nanotubes (CNTs), graphene and other carbon nanomaterials (CNMs) with their unique physical and structural properties [1–4] are promising candidates for a variety of electronic devices, sensors and flexible display applications. [5–9] For the industrial manufacturing of CNMs-based devices, a low-temperature, rapid and large area synthesis is a main point of technology. A development of low-temperature process of CNMs growth onto the silicon substrates would pave the way for the direct synthesis of CNMs onto glass and plastic substrates. One of the most perspective methods of low temperature synthesis of CNMs is the plasma-enhanced chemical vapor deposition (PECVD), because the presence of highly reactive plasma environment decreases the activation energy of the CNTs growth process [10]. One of the most popular sources of high density plasma applied in PECVD to grow CNMs is a microwave radiation [11–13]. Generally transition metals or their compounds are required to use as catalyst to produce CNTs by PECVD methods [10,11,13,14]. Chang, et al. [11] converted Ni catalyst from film into particles by microwave H2/N2 plasma and after that he used CH4/H2 plasma to realize a CNT growth at a temperature of 250°C. Lu, et al. [13] used Co catalyst prepared by sol-gel method to grow CNMs, where the samples were heated up to 280~330°C by Ar/CH4 or Ar/He/CH4 microwave plasma.

Microwave plasma CVD (MPCVD) also is maybe used for graphene films synthesis. Recently, few works using MPCVD exhibited a capacity to synthesis graphene at low temperatures. Kim, et al [12] examined the formation of the graphene-based films on the copper and aluminium foil using Ar/H2/CH4 gas flow mixture with microwave powers of 3 to 4.5 kW. Malesevic, et al. [15] used CH4/H2 microwave plasma with maximum input power of 2 kW to grow few-layer graphene (FLG). These former methods showed difficulties in synthesis of monolayer graphene, and graphene was synthesized at a relatively high temperature.

In this study, multi-walled CNTs and FLG sheets have successfully grown on Si substrates and polyimide substrates at relatively low temperature of 230~260°C by the microwave-excited surface wave plasma technique. Graphite-encapsulated Ni nanoparticles have been used as the catalyst for growing CNMs in NH3/CH4 or NH3/O2/CH4 plasma. It has been found that bias voltage and nature of the substrate can greatly influence the CNMs structure.

2. EXPERIMENTAL SETUP
In this work CNMs have been obtained by MPCVD technique without extra heating. Schematic draw of experimental device is presented in Fig. 1.
The microwave-excited surface-wave plasma has been produced in the stainless steel cylindrical vacuum chamber with 400 mm diameter by introducing 2.45 GHz microwave through a quartz window via slot antennas [13]. Although no heating stage is applied, due to the heating effect of the plasma itself, the substrate would be typically heated up to 230 ~ 260 °C, depending on the type of plasma, introduced power and whether bias voltage is applied or not. The substrate temperature has been measured by the thermo-couple in time of plasma-treatment process.

The catalytic particles have been prepared by DC arc-discharge method [16]. Graphene-encapsulated Ni nanoparticles (GNN) have been dissolved into the ethanol. This solution has been dropped with a pipette onto a cleaned (100) n-type silicon wafers and polyimide sheets. The substrates had the square form with 5 mm length of the side. Then, these substrates were evacuated in the vacuum chamber and processed by plasma. Two treatment steps were carried out. First, ammonia plasma has been applied within five minutes as pretreatment. At this stage pulsed bias voltage from –100 V to +25 V (ion current density is 15.4 and 0.8 mA/cm² respectively) has been applied with frequency of 500 Hz. The result of this treatment is appearance of defects on the graphene layers surrounding Ni core of catalytic particles. Secondly, NH₃/CH₄ (100/30 sccm) or NH₃/O₂/CH₄ (100/3/30 sccm) plasma post-treatment has been used within 30 minutes to grow CNMs. During the post-treatment we applied pulsed bias voltage from –30 V to +40 V (ion current density is 32 and 0.07 mA/cm² respectively) with frequency of 500 Hz. To avoid increasing of substrate temperature higher than defined value we made a break in plasma process after 15 minutes of treatment. Input microwave power has been 700 W; working pressure has been 20 Pa during both steps.

High-resolution transmission electron microscopy (HRTEM) JEOL JEM-2100F instrument at an operating voltage of 200 kV has been used to analyze morphology and detailed structure of the obtained CNMs. The specimens for TEM analysis have been prepared by dissolving the CNMs detached from the substrate in ethanol and further dropping solution on a 3-mm copper grid. Original morphology of samples has been analyzed by field emission type scanning electron microscope (FE-SEM) JEOL JSM 6320-F

3. RESULTS AND DISCUSSION

In this study we investigated effect of substrate and bias voltage on the CNMs growth.

Figure 2 show TEM images of CNMs obtained on the Si and polyimide substrates respectively in the case when bias voltage applied. It is clearly seen there that in the case of Si substrate (Fig. 2a) a lot of bamboo-like multiwalled CNTs with closed ends are observed. The typical lengths of these CNTs ranged from 200-300 nm to several microns and diameters within 15-25 nm roughly corresponding to the typical sizes of the catalytic Ni grains. HRTEM pictures (Fig. 2b) illustrate the wall of CNTs consisting of many layers of carbon sheets, with the average value of interlayer spacing of 0.34 nm.

CNMs grown on the polyimide substrate are presented in Fig. 3. It is seen that CNTs and FLG sheets are formed. CNTs have almost the same parameters, as in the case of Si substrates. Figure 3b illustrates an example of carbon...
sheets with graphene-like structures, having a characteristic size of several micrometers. The highest resolved image easily reveals the crystalline structure of the material. The fast-Fourier transform also clearly shows crystalline structure of the sample.

Without bias voltage it is seen large areas with amorphous carbon and corrosion films on the Si substrate. There is no formation of CNMs in this case except small amount of curly nanotubes with amorphous structure of walls (Fig. 4a). On the polyimide substrate, opposite, a lot of FLG sheets with typical size of few square micrometers are formed (Fig. 4b).

Such difference in structure of CNMs synthesized on different substrates can be explained by presence of surface charge in the case of polyimide substrate even when bias voltage was not applied. This charge can partially compensate the absence of bias voltage and change the energy of products coming from plasma on the surface of samples.

From Fig. 5 difference of the surface morphology between the untreated and plasma modified samples are observed. The initial surface with deposited GNN before plasma treatment has highly dispersed and uniform structure. However, after plasma modification, initial GNN become rarefied because of etching effect of plasma and the CNTs islands with typical size of few square micrometers are formed.

These results demonstrate that ammonia/methane MPCVD treatment with ammonia pretreatment is an effective approach, which can ensure low temperature growth of CNMs using graphene-encapsulated Ni nanoparticles as catalyst.

---

Fig. 4. TEM pictures of CNMs grown without bias voltage: a. – Si substrate; b. – polyimide substrate.

---

Fig. 5. FE-SEM pictures of: a. – untreated GNN; b. –CNMs grown on the Si substrate at low bias voltage.
4. CONCLUSIONS

In this work, a possibility of growth of CNTs and FLG sheets on the polymer substrates at relatively low temperature of 230 ~ 260 °C by MPCVD technique has been demonstrated. The results of SEM analysis illustrate the significant changes of morphology after plasma treatment of surface. The results of HR-TEM investigations show the greatly influences of bias voltage and nature of the substrate on the structure of grown CNMs. The origin of the obtained CNTs and FLG sheets will be further investigated in future experiments.

5. ACKNOWLEDGMENTS

This work was supported in part by a Grant-in-Aid for Scientific Research (Grant No. 2110010) from the Japan Society for the Promotion of Science (JSPS).

REFERENCES


(Received January 10, 2012; Accepted April 10, 2012)