The Effect of Substrate on the Low-Temperature Carbon Nanomaterials Growth by Microwave Excited Surface-wave Plasma Chemical Vapor Deposition

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Abstract. Multi-walled carbon nanotubes (CNTs) have been successfully grown on Si and polyimide substrates at temperature of 230~260°C by the microwave-excited surface wave plasma technique. Graphene-encapsulated nickel nanoparticles have been used as the catalyst for growing CNTs in NH₃/CH₄ plasma. The optimal gas flow mixture ratio and bias voltage for this type of plasma were investigated. High-resolution transmission electron microscopy and Raman spectroscopy investigations show similar results for CNTs grown on the Si and polyimide substrates.

1. Introduction
Carbon nanotubes (CNTs) have become of keen interest to material scientists since their discovery in 1991 [1]. CNTs have different potential applications such as molecular electronics [2], sensors [3, 4], field emission devices [5] and solar cells [6] owing to their combinations of chemical, physical and mechanical properties [7, 8]. The manufacturing of such devices requires growth of CNTs at low temperature where the structure and chemical composition of the functional materials remain unaltered. It is possible to produce CNTs by several methods [9-11] but one of the most promising ways to realize low temperature growth of carbon nanomaterials (CNMs) is the plasma-enhanced chemical vapor deposition (PECVD), because the presence of highly reactive plasma environment decreases the activation energy of the CNT growth process [12]. One of the most popular sources of high density plasma applied in PECVD to grow CNTs is a microwave radiation.

Generally the PECVD methods require a metal catalyst to produce CNTs. Transition metals or their compounds are generally used as catalyst [12-16]. Yamazaki, et al. [14] have grown CNTs at temperature below 400°C by a remote PECVD with Co catalytic nanoparticles deposited by the impactor method on the TiN/SiO₂/Si substrates. At this experiment has been used the gas mixture of methane and hydrogen. In the reference [15] the Co catalyst prepared by sol-gel method has been used to grow CNMs, where the samples were heated up to 280~330°C by Ar/CH₄ or Ar/He/CH₄ microwave plasma. Chang, et al. [16] converted Ni catalyst from the film into particles by microwave H₂/N₂ plasma and after that he used CH₄/H₂ plasma to realize the CNTs growth at the temperature of 250°C.

In this study, multi-walled CNTs (MWCNTs) have successfully grown on Si substrates at temperature of 230~260°C by the microwave-excited surface wave plasma technique. Graphite-encapsulated Ni nanoparticles (GNNs) have been used as the catalyst for growing CNTs in NH₃/CH₄
plasma. We chose ammonia as a carrier gas because of its chemical activity. During the growth process, NH$_3$ may generate atomic hydrogen species providing etching effects for the growing amorphous carbon [17]. Because of these effects NH$_3$ helps to maintain surface of metal catalyst active [18]. It has been found that the gas mixture ratio NH$_3$/CH$_4$ and bias voltage can greatly effect on the CNTs growth. The threshold values of CH$_4$ concentration and bias voltage of substrate stage for CNTs growth have been investigated. We have also demonstrated the CNTs growth on the polyimide substrate using the present method.

2. Experimental

In this work, we used a microwave surface wave plasma device as shown in Figure 1. The polished (100) n-type silicon wafers and polyimide sheets covered with GNNs produced by DC arc-discharge method [19] have been placed on the stage located at 110 mm from the quartz window of the microwave plasma device to activate GNNs by a ammonia plasma pretreatment, where a 2.45 GHz microwave was introduced through a quartz window via slot antenna [15] at pressure of 20 Pa with the maximum power of 700 W. During the first stage of CNTs growth, the substrate stage was biased negatively by a pulsed squared wave with amplitude of −100 V at a frequency of 500 Hz. After the pretreatment, CNTs growth has been realized by NH$_3$/CH$_4$ plasma post-treatment with a low bias voltage at −30 V. Although no heating stage has been applied, due to the heating effect of plasma itself, the substrates were heated up to 230 ~ 260 °C depending on the plasma conditions. The temperature of the sample holder has been measured by a thermocouple during the plasma process. Different NH$_3$/CH$_4$ gas flow mixtures (from 100/1 to 100/50 sccm) have been introduced to the microwave plasma system to study the optimal gas flow ratio for CNTs growth.

![Figure 1. Scheme of the surface-wave plasma device.](image)

Excited atomic and molecular species have been measured during the CNTs growth process by the optical emission spectroscopy (OES) diagnosis, in order to study the correlation between the molecular species and CNTs growth. High-resolution transmission electron microscopy (HRTEM) JEOL JEM-2100F instrument at an operating voltage of 200 kV has been carried out to analyze morphology and detailed structure of the CNTs. The specimens for TEM analysis have been prepared by dissolving the CNTs detached from the substrate in ethanol. Raman spectroscopy has been also used to characterize CNTs grown on silicon and polyimide substrates using JASCO NR-1800 Raman spectrophotometer with Ar$^+$ ion laser at a wavelength of 514.5 nm.

3. Results and discussion

The typical OES spectrum of NH$_3$/CH$_4$ microwave plasma is shown in Figure 2a. It can be seen that line spectra due to methane fragments, such as CH at 430 and 390 nm and the hydrogen Balmer lines H$_\alpha$ at 656 nm, H$_\beta$ at 486 nm, and H$_\gamma$ at 434 nm, numerous H$_2$ molecular bands at 463 and 602 nm [20] are partly obscured by those due to ammonia. Emission band from NH species corresponding to
transitions at 336 nm, CN species corresponding to $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ transitions have been observed. There is no observation of $C_2$ radical emission from this spectrum. Hence, it is considered that carbon source for CNTs growth come from the CN violet system which has three strong sequences with heads at 421.6, 388.3, and 359 nm. The strongest CN emission peak at 388.3 nm increases with the CH$_4$ flow rate being increased and reaches a maximum at 30 sccm of methane and after that keep high intensity (Figure 2b). Hydrogen Balmer lines H$_\alpha$ at 656 nm (3d$^2$D $\rightarrow$ 2p$^2$P$^0$) and H$_\beta$ at 486 nm (4d$^2$D $\rightarrow$ 2p$^2$P$^0$) are not obscured by ammonia peaks and have been monitored with the variation of plasma conditions. The results of OES studies provided clues to the possible active species present in the plasma during the synthesis of CNTs but there is still a lack of information on the actual surface reaction of the catalysts.

![Figure 2](attachment:figure2.png)

Figure 2. a.– The typical OES spectrum of NH$_3$/CH$_4$ microwave plasma (gas flow mixture ratio is 100/30); b.– Effect of CH$_4$ flow rate on the intensity of CN emission peak at 388.3 nm (NH$_3$ flow rate fixed at 100 sccm).

It can be seen from HRTEM pictures that MWCNTs with the typical diameters around 5 nm and the typical lengths 50-60 nm start growing when the NH$_3$/CH$_4$ gas flow proportion is 100/20 sccm, but optimal gas flow mixtures of NH$_3$/CH$_4$ for this type of plasma is 100/30 sccm. In this case straight and curly CNTs are being formed with typical lengths 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.

In Figure 3a-b, the product typically exhibits tube-like structures with closed ends for both Si and polyimide substrates. The wall is made of many layers of carbon sheets, between which the lattice fringes of interplanar spacing can be clearly identified in the figure. The average value of spacing is 0.34 nm, which is close to the literature data [21]. In the case of polyimide substrate, MWCNTs with opened ends with diameters within 50 nm were also observed (Figure 3c).

![Figure 3](attachment:figure3.png)

Figure 3. CNTs obtained from NH$_3$/CH$_4$ plasma with gas flow ratio 100/30 sccm at -30 V.

a. – CNT with closed ends on the Si substrate; b. – CNT with closed ends on the polyimide substrate; c. – CNT with opened ends on the polyimide substrate.
Raman spectrum of CNTs grown on the Si substrate (Figure 4a) shows strong D and G-bands, which correspond to typical CNTs vibration modes. The bands are ascribed to the disorder-induced (D) mode at 1350 cm\(^{-1}\), the C-C stretching tangential (G) mode at 1582 cm\(^{-1}\), and the disorder-induced (D') mode at 1620 cm\(^{-1}\) [22]. The distinct shoulder of CNTs near 1620 cm\(^{-1}\) (D') originates from the A\(_{1g}\) tangential Raman mode for MWNTs [23]. The intensity of D-band peak is slightly stronger than that of G-band peak, which might be caused by defects of MWCNTs [24]. The similar results have been observed for CNTs synthesized on the polyimide substrate (Figure 4b).

Figure 4. Raman spectrum of the final product:
(a) – CNTs grown on the Si substrate; (b) – CNTs grown on the polyimide substrate.

4. Conclusions
The low-temperature growth of MWCNTs on the Si and polyimide substrates has been realized by microwave surface wave plasma CVD at temperature of 230 ~ 260 °C, where the graphene-encapsulated nickel nanoparticles were used as the catalyst for growing CNTs in NH\(_3\)/CH\(_4\) plasma. The optimal gas flow rate ratio and substrate bias voltage at the stage of post-treatment for CNTs growth have been investigated for ammonia/methane surface wave plasma plasma. HRTEM and Raman spectroscopy investigations show similar results for CNTs grown on the Si and polyimide substrates. Hereby, this work shows the possibility of CNTs growth from NH\(_3\)/CH\(_4\) environment at a relatively low temperature directly on polymer substrate.

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