Effects of thickness of Ni layer deposited on glass substrate on the growth and emission properties of carbon nanotubes

Jae-hee Han a,*, Ha Jin Kim a, Min-Ho Yang a, Cheol Woong Yang a, Ji-Beom Yoo a, Chong-Yun Park b, Yoon-Ho Song c, Ki-Soo Nam c

a School of Metallurgical and Materials Engineering, Sungkyunkwan University, 300 Chunchun-Dong, Jangan-Gu, Suwon 440-746 South Korea
b Department of Physics, Sungkyunkwan University, 300 Chunchun-Dong, Jangan-Gu, Suwon 440-746 South Korea
c Microelectronics Technology Laboratory, ETRI, 161 Kajong-Dong, Yusong-Gu, Taejon, South Korea

Abstract

Vertically aligned carbon nanotubes were grown on the Cr-coated glass substrate with different thickness of Ni catalyst layer at low temperatures (~600 °C) using plasma-enhanced hot filament chemical vapor deposition (PEHFCVD). The diameter of carbon nanotubes grown for 14 min increased from 32 to 113 nm as the thickness of Ni layer increased form 10 to 100 nm. However, the diameter of carbon nanotubes grown for 34 min was almost same irrespective of Ni layer thickness. The emission characteristics of carbon nanotubes (CNTs) were dependent on the diameter of carbon nanotubes and substrate. Turn on electric field, \( E_{on} \), increased from 6.9 to 9.6 V/\( \mu \)m as the diameter of carbon nanotubes increased from 44 to 64 nm. \( E_{on} \) of carbon nanotubes without Cr buffer layer was lower than that of carbon nanotubes with Cr layer. The electron emission from carbon nanotubes grown on Si substrate was larger than that of carbon nanotubes on glass substrate with the same Cr and Ni layer.

1. Introduction

Since the first discovery of carbon nanotubes (CNTs) in 1991 [1], CNTs have received a considerable attention because of the prospect of new fundamental science and many potential applications. CNTs are promising candidates, particularly, for cold cathode field emitter because of their unique electrical properties, high aspect ratios and small radii of curvature at their tips [2–6]. For applications such as flat panel displays, vertical alignment, emission properties, low temperature growth, and size control of CNTs are important.

Recently, much effort has been devoted to synthesis of vertically aligned CNTs on various substrates such as Si, mesoporous silica and glass using thermal CVD [7] and plasma-enhanced hot filament chemical vapor deposition (PEHFCVD) [8]. Transition metal catalyst such as Ni and Fe is essential in the nucleation and growth of aligned CNTs. The size of the catalytic particles determines the size of CNTs. The role of metal catalyst in the growth process was investigated [9,10]. However, effect of thickness of Ni layer and the Cr buffer layer on the growth and electron emission characteristics of CNTs has not been reported yet.

In this report, vertically aligned CNTs were grown on the Cr-coated glass substrate with different thickness of Ni catalyst layers at low temperatures (~600 °C) using plasma-enhanced hot filament chemical vapor deposition (PEHFCVD). A thin Cr layer was used as a buffer layer to improve the adhesion of CNTs to the substrate. Effect of thickness of Ni layer deposited on the Cr buffer layer on the growth and emission characteristics of CNTs was investigated. Electron emission from CNTs grown on Si substrate was also studied and compared to that of CNTs grown on glass substrate.

2. Experiments

The growth of vertically aligned CNTs was carried out using plasma-enhanced hot filament chemical vapor deposition (PEHFCVD) system (Mater. Sci. Technol. Model CNT2000). A schematic diagram of the PEHFCVD system was shown in Fig. 1. Acetylene (C₂H₂) and ammonia (NH₃) gas were used as a carbon source and catalyst, respectively. A DC plasma was employed in this work to
deposit vertically aligned CNTs. A thin Cr buffer layer and Ni catalytic layer were deposited by electron beam evaporation. The deposition of Cr and Ni layer was carried out at 50 °C. The thickness of Cr layer was 1000 Å. The thickness of Ni layer changed from 10 to 100 nm. Si substrate was also used to compare the growth and emission characteristics of CNTs with those of CNTs on glass substrate. SiNₓ layer was deposited on Si substrate before Cr buffer layer deposition using plasma-enhanced chemical vapor deposition (PECVD). Flow rate of SiH₄, NH₃, N₂ and H₂ were 7, 105, 200 and 100 sccm, respectively. Prior to CNTs growth, the substrate was cleaned in trichloroethylene, acetone, methanol for 10 min, and rinsed in deionized water to remove organic contaminants. The substrate was transferred to the chamber and pumped down below 2 × 10⁻⁵ Torr by a mechanical and a diffusion pump. After the chamber pressure reached 2 × 10⁻⁵ Torr, NH₃ was introduced into the chamber. After the working pressure had been stabilized, the power to the tungsten filament coil and to the DC power supply were turned on to generate heat and plasma. The bias voltage for plasma generation changed from 400 to 650 V. The pre-treatment for surface etching of Ni layer was conducted by NH₃ plasma for 1–4 min. Then C₂H₂ was introduced into the chamber for the growth of CNTs. The substrate temperature was measured using thermocouple and pyrometer (IR-GPD, CHINO).

The morphology of CNTs was characterized by scanning electron microscopy (SEM). Electron emission was measured as a function of applied voltage using phosphor-coated ITO anode in the vacuum chamber.

3. Results and discussion

We investigated the effect of Ni layer thickness on the diameter of carbon nanotubes (CNTs). Ni layer thickness changed from 10 to 100 nm. The Ni pre-etching was performed under the condition that the working pressure was 3 Torr, the flow rate of NH₃ was 120 sccm, the filament current 14.1 A, the plasma bias voltage and current were 440 V and 0.06 A, the etching time was 1 min. After nickel etching with NH₃, C₂H₂ was introduced for CNTs growth, the flow rate of C₂H₂ was 30 sccm, the filament current was 11.1 A, the plasma intensity during growth was 580 V and 0.14 A, and the growth time was 14 and 34 min.

Fig. 1. Schematic diagram of plasma-enhanced hot filament chemical vapor deposition (PEHFCVD) reactor.

Fig. 2. SEM images of carbon nanotubes grown on different Ni thickness for different growth time: (a) 14 min, (b) 34 min.
The SEM images of series of samples are shown in Fig. 2. As the as-deposited thickness of Ni layer increased from 10 to 100 nm, the mean diameter of CNTs increased from 32 to 113 nm for the 14-min growth. This may be attributed to the grain size effect. The CNTs were grown along the grain of Ni so that the diameter of CNTs is determined by the grain size of Ni. As Ni layer thickness increased, the grain size in nickel film becomes larger. In case of Ni 100 nm thickness, the SEM image does not seem to be carbon nanotube but carbon nanoparticle, which was shown at the initial stage of CNTs growth [11]. However, for the 34-min growth, the diameter of CNTs grown on different Ni thickness is almost same (∼41 nm) irrespective of the nickel layer thickness. The diameter of CNTs grown for a relatively long time does not seem to be affected by the initial grain size of nickel. The bundles of thin CNTs appeared in the sample with 100-nm Ni thickness. Growth of CNT was controlled by tip-growth model in PEHFCVD [8]. As the growth of CNT proceeds, the Ni tip exhausts and becomes small. The diameter of CNT grown for longer time becomes smaller and the effect of Ni layer becomes negligible. The variation of the diameter of CNTs with the as-deposited Ni layer thickness under the different growth time 14 and 34 min was shown in Fig. 3.

The effect of diameter of CNTs and substrates on the emission characteristics of CNTs was investigated and shown in Fig. 4. As shown in Fig. 4, turn-on electric field intensity ($E_{\text{to}}$) of CNTs increased with the diameter of CNTs. The $E_{\text{to}}$ of the CNTs grown on Ni (30 nm)/Cr/glass for 34 min was 6.9 V/µm but that of CNTs grown on Ni (30 nm)/Cr/glass for 14 min was 9.5 V/µm. The diameter of CNTs grown for 14 and 34 min was 64 and 44 nm, respectively. From the image of CNTs, the shape of CNTs grown for 34 min is sharper than that of CNTs grown for 14 min. The decrease in $E_{\text{to}}$ may be due to the smaller curvature of tip of CNTs.

The difference in electron emission characteristics of CNTs grown with or without chrome buffer layer is also shown in Fig. 4. Cr buffer layer is employed between substrate and Ni catalytic layer to improve the adhesion of Ni layer to the substrate. The emission of the sample without Cr buffer layer is larger than that of the sample with Cr buffer layer. From the emission characteristics of CNTs with and without Cr layer, further investigation on another buffer layer such as TiN is required. Emission from the CNTs grown on Si substrate begins at the lower $E_{\text{to}}$ than emission from the CNTs grown on glass substrate which has the same thickness of Ni and Cr layer. Dependence of emission characteristics on the substrate may be attributed to the geometry of CNTs but it needs further investigation.

### 4. Conclusion

Vertically aligned carbon nanotubes were grown on the Cr-coated glass substrate with a different thickness of Ni...
catalyst layer at low temperatures (< 600 °C) using PE-HFCVD. The diameter of carbon nanotubes increased with as-deposited thickness of Ni for growth time of 14 min. However, for 34 min, that of carbon nanotubes is almost same. Turn on electric field, $E_{in}$, increased from 6.9 to 9.6 V/μm as the diameter of carbon nanotubes increased from 44 to 64 nm. $E_{in}$ of carbon nanotubes without Cr buffer layer was lower than that of carbon nanotubes with Cr layer. Electron emission from the carbon nanotubes grown on Si substrate was larger than that of carbon nanotubes on glass substrate with the same Cr and Ni layer.

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References