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Original Article

Hot-filament CVD Growth of Vertically-aligned Carbon Nanotubes on Support Materials for Field Electron Emitters

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Abstract: Carbon nanotubes are used in different applications such as energy storages, electronic devices. For these applications, a direct assembly of the vertically-aligned carbon nanotubes (VACNTs) on electrically conducting substrates is of interest. In this work, we report a direct growth of the VACNTs on several substrates by using hot-filament chemical vapor deposition (hot-filament CVD) and a catalytic buffer-layer structure. The buffer layer was the aluminum (Al) thin film used together with iron (Fe) as the catalyst. It was found that the Al underneath layer was necessary for obtaining the VACNT forests with high purity and good contact. The as-fabricated VACNT/support-material structures are of the object to test field electron emission properties. Characterization results of the VACNT samples demonstrated a promising application for the field emission in terms of the high emitting currents.

Keywords: Carbon nanotubes, hot-filament CVD, field electron emission, catalysis.

1. Introduction

Carbon nanotubes have potential applications, including interconnects for supercapacitors, fuel cells, electron emitting devices [1-5]. For these applications, a direct assembly of the vertically-aligned carbon nanotubes (VACNTs) on electrically conducting substrates is mostly needed. The most obvious method to obtain such structures is the direct growth of the carbon nanotubes on conducting substrates. In recent years, the VACNT synthesis has significantly advanced. Key points have been attributed to not only method-to-grow but also catalytic material preparedness. The choice and the

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method to transform the catalyst into the substrate are also important to the success of the VACNT growth. Using suitable catalysts along with CVD methods, some scientific groups have achieved good productions of the VACNTs [1, 2-6].

In most of the cases, the buffer layer enhanced catalyst is the prerequisite condition to grow good carbon nanotubes. The underneath layer is interpreted as a diffusion barrier and to keep the catalytic properties sustainable. The underneath layer also has been used to control the CNT density by its thickness and structure [7]. As previously mentioned, the CVD methods have been the most widely used to cultivate the VACNTs on the silicon and the metals as well. The VACNT growth on metals is more difficult because of the interactive reactions of the substrates with catalyst itself in the high temperature condition during a CVD process which is detrimental to the catalyst and the subsequent growth. Hiraoka et al. have developed a water-assisted CVD process to grow the VANCTs on the metal foils made of the nickel-based alloys with chromium and iron [8]. Talapatra et al. have reported the VACNT synthesis on Inconel 600, and possibly on the metal substrates using the ferrocene-xylene CVD system. However, the quality and the structure of the as-grown carbon nanotubes have not been interpreted clearly [9]. The VACNTs produced on kitchen aluminum foils by Yoshikawa's group [10], with film thickness both were less than 50 μm. On the other hand, Bayer et al. have shown that using low temperature plasma-assisted CVD enables the CNT formation. However, the low temperature CVD process has compromised the graphitic structure of the carbon nanotubes [11]. In brief, for the CNT-based electronic devices, one has the better growth of the VACNTs, the better performance is achieved. Therefore, seeking VACNTs synthesis is still of interest.

In this work, we focused on the catalyst structure and its effects on the VACNT thickness and morphology. The catalyst to be used includes the iron thin film deposited on the Al underneath layer and with the substrates including or silicon and the metal foils. As-fabricated VACNT/substrate structures are of the object to test the field electron emission properties. Testing results of the VACNT samples demonstrated promising field emission characteristics in terms of high emitting currents and good stability.

2. Materials and Methods

The VACNT growth was carried out by using a hot filament CVD method as described in [12]. In short, the feedstock gas, a CH_4/H_2 mixture is introduced into the CVD chamber. A bias voltage over tungsten-made filaments is gradually increased and the filament temperature was elevated to about 2200 - 2500^{o}C. Rapid insertion of the growth substrate into the working zone (17-mm beneath the tungsten filament) is followed and the substrate heating occurs rapidly through radiant heat transfer. Carbon nanotubes start growing since the substrate reaches about 600^{o}C, however the eventual growth is maintained at about 700–750^{o}C. The VACNTs were produced by a three-step process consisting of the catalyst deposition, the pre-treatment, and the CVD process. For the silicon substrate, the polished, n-type silicon (100) wafers were used. It is to be noted that there exists native silicon oxide thin film in each sample, the thickness of about 2 nm. For the metal substrates, Stainless steel (SS), and Titanium (Ti), Cooper (Cu), thickness of 250–500 μm from Sigma supplier were used. These metal foils were cleaned ultrasonically in acetone/isopropyl for 15 min each before the other following experimental steps. To produce the catalytic thin films, the sequential sputtering in the Argon atmosphere (2.5×10^{-2} Torr) was employed. The nominal thickness of Al, Fe were estimated from the pre-determined deposition rates. The Fe thin film used for growing CNTs was from 1÷5 nm. In the second step, the catalyst was annealed at 400÷500^{o}C in the air atmosphere for 10 minutes by using a thermal furnace. This process transformed the catalyst thin films into high-density and nanosized-particles that was

needed for the VACNT production [13]. The heat treatment also allowed iron particles being oxidized purposely and hence prevent silicide formation that deactivates catalytic properties [14].

Figure 1 shows typical scanning electron microscopy (SEM) images of the catalyst after the pretreatment. In appearance, the buffer layer (Al) and the substrate both impact on the resulting catalyst. Without the Al layer, the large nanoparticles and low density is obtained. With the metal substrate, it seems the nanoparticle formation is inferior to that of the silicon substrate. For the silicon, the Fe/Al (1nm/10nm) catalyst films are strongly restructured and broken into nanosized particles with a narrow distribution of sizes. The catalytic nanoparticle is about 10–20 nm in diameter. The experiments confirmed the pretreatment conditions had a strong effect on the nanoparticle density. Indeed, if the thermal annealing was done under low temperature, the catalyst was restructured to clusters rather than the particles. On the other hand, high temperature led to large particles and less dense caused by heat induced coalescence.

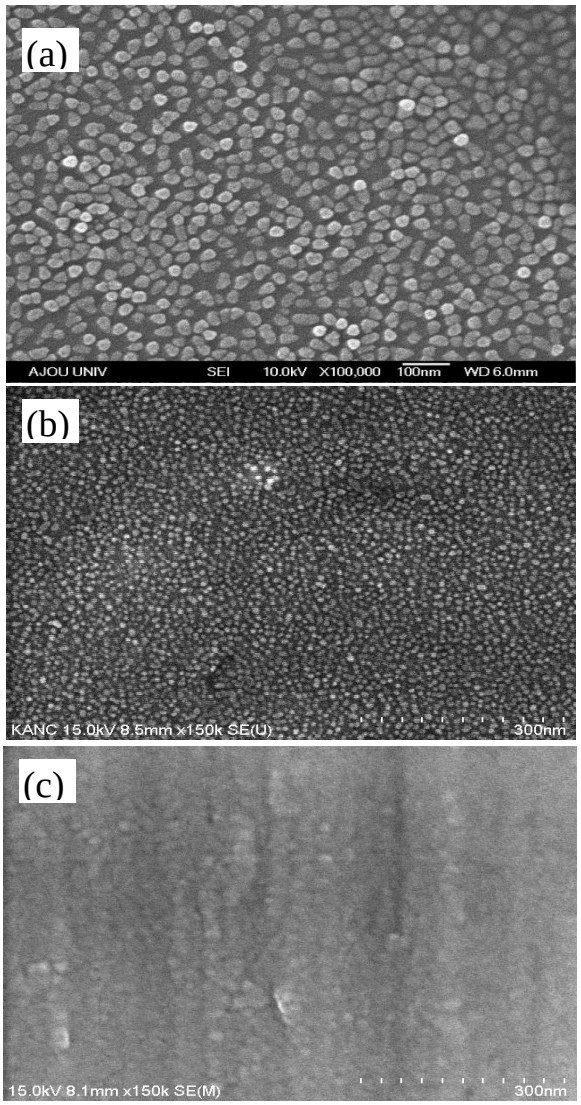

Figure 1. SEM images of typical catalytic thin films after pretreatment for 10 minutes: (a) Fe-3nm/Si, 500°C; (b) Fe-1nm/Al-10nm/Si, 500°C; (c) Fe-5nm/Al-40nm/Titanium,450°C.

The VACNTs were synthesized by the hot-filament CVD method using 30-Torr mixtures of methane (20 SCCM) and hydrogen (30 SCMM) as feedstock, the growth time of the same, 9 minutes. The hot-filament CVD underlines the decomposition of hydrocarbon and hydrogen at highly elevated temperature (2200–2500^{o}C), which is decoupled to the growth substrate temperature (700–750^{o}C). This facilitates the VACNT growth in high-temperature hydrocarbon disassociation but not degrade the catalyst yield. Table 1 shows the experimental conditions to grow the VACNTs. The VACNT films were examined by a scanning electron microscope (SEM), Thermal gravimetric analysis (TGA), and Raman spectroscopy.

Field emission (FE) measurements were carried out in a vacuum chamber with a pressure of about 5×10^{-6} Torr. Keithley-248 multi-source was used to supply voltage for the anode. The emission current was measured by Keithley-2001 multi-meter. FE data were acquired using LABVIEW software and a personal computer through a general-purpose interface bus interface (GPIB) card. Figure 2 depicts the measuring setup. The diode configuration was used to collect FE data in which flat aluminum pieces were employed as an anode and a cathode holder on which the VACNTs/support materials (silicon and/or metal) were based. The electrical contact between the back-side of the support materials and the aluminum cathode holder was secured by the silver conductive paint. The anode and the cathode were separated by a spacer made of the insulator materials. The gap refers to the distance between the anode and the VACNT top-surface. We also installed a CCD camera which was connected to PC, to monitor and record either the emission image or any changes on the cathode surface in the real test mode. The field emission measurements were repeated at least tens of times by ramping bias voltage up and down. The electric field was calculated to be the anode voltage divided by the gap. Current densities were estimated from the net currents and the top-surface areas of emitters. The turn-on field refers to an electric field necessary to extract 100 nA of emission current following the conventional definition.

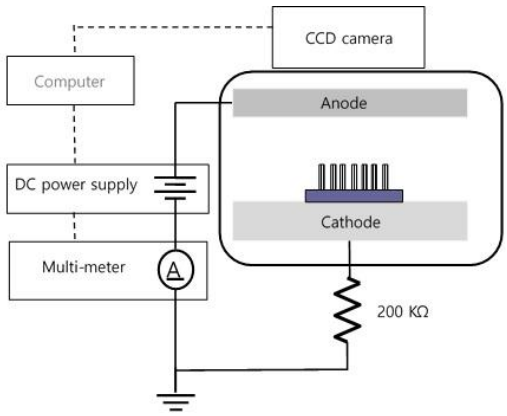

Figure 2. Field emission measuring setup.

3. Results and Discussions

Figure 3 shows typical SEM images of as-produced VACNTs (the surface and cross-section viewing) on typical substrates including the bare silicon with and without the Al buffer layer, and the Ti substrates. The VACNT thickness depends on the catalyst arrangement. Roughly, for the Si substrate without the Al underneath layer, the VACNT thickness was 180–200 μm; the effective

growth rate of about 20 μm/min. This observation is similar to those of the VACNTs/metal substrates. The preliminary result showed that the Al layer has good enhancement for the VACNT growth in term of the growth rate. The VACNTs are grown better on the silicon substrate with the Al buffer layer. The averaged VACNTs thickness is measured about 850÷1100 μm (the effective growth rate of about 100–120 μm/min). We also found that the catalyst topographies have a strong effect on the VACNT structure. Observing high resolution SEM images shows well-aligned nanotubes as a result of the dense growth and high-yield nucleation (Figure 3b). The nanotube diameter (outer) was estimated at about 15 nm ± 3 nm.

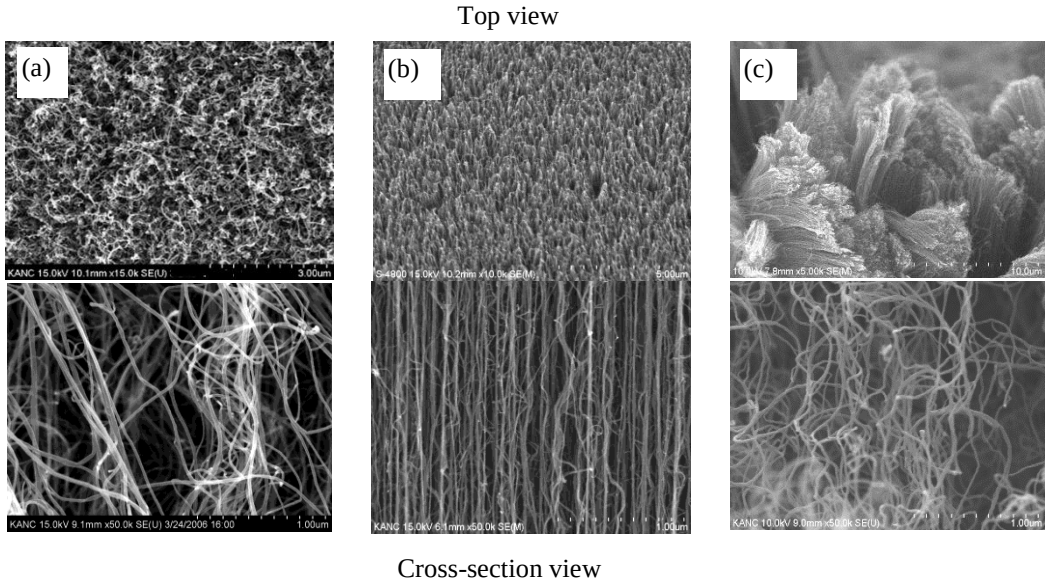

Figure 3. SEM images (up: top view; down: cross-section view) of carbon nanotubes produced on substrates (up): (a) bare Si; (b) Al/Si; (c) Al/metal (Ti).

It is plausible that the Al underneath layer may play as a diffusion barrier which prevents iron-based loss. Without the diffusion barrier, iron can diffuse into silicon at elevated temperatures so that an iron-silicide layer which does not support the VACNT growth can be formed [15]. Aluminum may also play a supportive component to prevent the nanoparticle aggregation which had the negative effects on the VACNT growth. Our previous experiment with silica- or alumina-supported Fe catalysts showed that alumina could act as a stable matrix material which keeps the nanosized Fe from coalescence.

The as-fabricated VACNTs were used for field emission applications, it is required the as-prepared carbon nanotubes need to be highly pure, less amorphous and carbonaceous impurities. In the experiments, the VACNTs purity and contamination were characterized by TGA, Raman spectroscopy (the data were not shown here). In general, the as-produced VACNTs have the multi-wall structure and the high purity.

The VACNT/substrates (cathodes) are subject to field emission tests to understand their field emission properties. For the FE testing, the VACNTs cathode with 2-mm in diameter was used. The anode to the VACNT top-surface distance of ~1500–1700 μm, depends on the particular samples. Figure 4(a) showed *I-E* curve, net current (mA) versus electric field (V/μm), of the VACNT cathodes. The emission-current density was estimated from the surface area of 3.14×10^{-2} cm^2. Table 2

summarizes the field emission results; showing quite good emission (turn-on field and high-current emitting capability) from three VACNT cathodes. One can obtain a turn-on field < 0.7 V/μm, 1-mA emitting currents at the applied field < 1.7 V/μm from the as-fabricated VANCTs. In addition, it can be seen that the VACNTs/Al/Si shows the lowest turn-on field (0.57 V/μm), significant better compared to those of the VACNTs/bare silicon and the VACNTs/Al/Ti. Previously individual CNTs are confirmed to be good emitters due to their high aspect ratio in shape. However, the CVD growth produced the CNTs as a "carpet", nanotubes are entangled each other. This results in the screen effect that is reduced the enhanced field effect of carbon nanotubes [16,17]. Because of the well-aligned carbon nanotubes on the VACNTs/Al/Si, the screen effect may impact lesser and therefore is assumed to contribute to the electron extraction at the lower applied voltage.

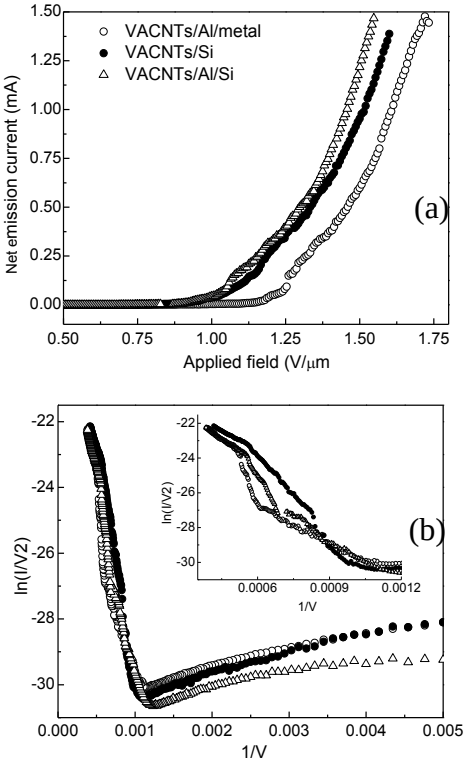

Figure 4. (a) *I-V* characteristics of the VACNTs/Ti structure
and (b) Corresponding F-N plots; inset: F-N plot in a shorter range of 1/V values.

A Fowler-Nordheim (FN) plot, $\ln(I/V^2)$ versus $1/V$, is shown in Figure 4(b). Generally, a linear *F-N* plot is attributed to a quantum tunneling process through a potential barrier that is thinned because of electric field. It can be observed the linearity of the F-N plots in Figure 4(b), so the measured electron currents obey the field emission law. Theoretically, F-N equation is given in terms of the emission current I in ampere, emission area A in square-meter, applied bias voltage V in volt, cathode-anode gap d in meter, work function ϕ (5 eV) in eV as following:

$$I = A\frac{1.42\times10^{-6}}{\phi}\beta^2\left(\frac{V}{d}\right)^2\exp\left(\frac{10.4}{\sqrt{\phi}}\right)\exp\left(-\frac{B\phi^{1.5}d}{\beta V}\right)$$

where β is the field enhancement factor, and $B = 6.44\times10^9$ $VeV^{-1.5}m^{-1}$ is a constant. Therefore, the plot of $\ln(I/V^2)$ with respect to $1/V$ becomes linear, and the slope is given by $-B\phi^{1.5}d/\beta$. Using the slope that was deduced by fitting the linear segment of the *F-N* plot to a straight line together with the known values for *d* and *B*, we estimated the field enhancement factor β (Table 2). The VACNTs/Al/Si shows the largest value of the field enhancement (4635). However, the field enhancement calculation by the F-N plot fitting is tricky. It depends on the segment to be fit that is graphic influenced, the β value can deviate correspondingly. Further, inset in Figure 4(b) demonstrates the F-N plot in 1/V range of 0–0.012. It shows some sections other than a single linear segment. The multi-section in the F-N plots is complicated and may originate from multiple causes, for example, space charge, contact resistance, thermionic emission. These issues are being studied further.

Table 1. The experimental parameter and the resulting VACNTs.

Catalyst/ Substrate	Pretreatment* (°C)	Substrate temp. (°C)	CNT length (μm)	Growth rate (μm/min)
Fe-3nm/Si	500	750	180–200	20–22
Fe-3nm/Al-10nm/Si	500	750	850–1150	95–125
Fe-4nm/Al-30nm/SS	450	700	95–120	10–13
Fe-4nm/Al-40nm/Ti	450	700	85–120	9–13
Fe-4nm/Al-50nm/Cu	450	700	105–150	11–16

* Pretreatment: 10 minutes

Table 2. FE testing results

Catalyst/ Substrate	VACNT thickness (μm)	Turn-on field* (V/μm)	Applied Field to extract 1-mA current (V/μm)	Field enhancement (□)
Fe-1nm/Si	185	0.67	1.52	3976
Fe-3nm/Al-10nm/Si	950	0.57	1.46	4635
Fe-4nm/Al-30nm/SS	105	0.65	1.61	3852

* Turn-on field: Necessary field to extract 100-nA emitting currents

4. Conclusions

We herein presented the VACNTs growth on some support substrates by using hot-filament CVD. The Aluminum underneath layer is important to the good growth. For the metal substrates, Fe-4nm/Al-40nm thin films and pretreated at 450°C lead to the best growth of the VACNTs with a thickness of about 180 μm. For the silicon substrates, Fe-3nm/Al-10nm and 500°C pretreatment are the proper choice, the VACNT growth of about 1100 μm in thickness. The as-fabricated VACNTs show good field emission, the turn-on fields < 0.9 V/μm, 1-mA emitting currents can be obtained at applied fields < 1.8 V/μm.

Obtained results of the VACNT samples demonstrated a promising application in the field electron emitters in terms of the high emitting currents and good stability.

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References

[1] X. Li, M. Baker-Fales, H. Almkhelfe, N. R. Gaede, T. S. Harris, and P. B. Amama, Rational Modification of a Metallic Substrate for CVD Growth of Carbon Nanotubes, Scientific reports 8 (2018) 4349 – 4359.

[2] B. Kim, H. Chung, K. S. Chu, H. G. Yoon, C. J. Lee, W. Kim, Synthesis of vertically-aligned carbon nanotubes on stainless steel by water-assisted chemical vapor deposition and characterization of their electrochemical properties, Synthetic Metals 160 (2010) 584 – 587.

[3] Xiomara Calderón-Colón, Huaizhi Geng, Bo Gao, Lei An, Guohua Cao, and Otto Zhou, A carbon nanotube field emission cathode with high current density and long-term stability, Nanotechnology 20 (2009) 325707 - 325712.

[4] Rémi Longtin et al, Active vacuum brazing of CNT films to metal substrates for superior electron field emission performance, Sci. Technol. Adv. Mater. 16 (2015) 015005 – 015016.

[5] Sangjun Park et al, Carbon Nanotube Field Emitters Synthesized on Metal Alloy Substrate by PECVD for Customized Compact Field Emission Devices to Be Used in X-Ray Source Applications, Nanomaterials 8 (2018) 378 – 387.

[6] M. Morassutto, R.M. Tiggelaar, M.A. Smithers, and J.G.E. Gardeniers, Vertically aligned carbon nanotube field emitter arrays with Ohmic base contact to silicon by Fe-catalyzed chemical vapor deposition, Materials Today Communications 7 (2016) 89 -100.

[7] Lance Delzeit, Bin Chen, Alan Cassell, Ramsey Stevens, Cattien Nguyen, and M. Meyyappan, Multilayered metal catalysts for controlling the density of single-wall carbon nanotubes, Chem. Phys. Lett. 348 (2001) 368-374.

[8] T. Hiraoka, T. Yamada, K. Hata, D. N. Futaba, H. Kurachi, S. Uemura, M. Yumura, and S. Iijima, Synthesis of Single- and Double-Walled Carbon Nanotube Forests on Conducting Metal Foils, J. Am. Chem. Soc. 128 (2006) 13338 – 13339.

[9] S. Talapatra, S. Kar, S. K. Pal, R. Vajtal, L. Ci, P. Victor, M. M. Shaijumon, S. Kaur, O. Nalamasu, and P. M. Ajayan, Direct growth of aligned carbon nanotubes on bulk metals, Nature nanotechnology 1 (2006) 112 - 116.

[10] N. Yoshikawa, T. Asari, N. Kishi, S. Hayashi, T. Sugai, and H. Shinohara, An efficient fabrication of vertically aligned carbon nanotubes on flexible aluminum foils by catalyst-supported chemical vapor deposition, Nanotechnology 19 (2008) 245607 – 245612.

[11] B. C. Bayer, S. Hofmann, C. Castellarin-Cudia, R. Blume, C. Baehtz, S. Esconjauregui, C. T. Wirth, R. A. Oliver, C. Ducati, A. Knop-Gericke, R. Sch, A. Goldoni, C. Cepek, and J. Robertson, Support−Catalyst−Gas Interactions during Carbon Nanotube Growth on Metallic Ta Films, J. Phys. Chem. C 115 (2011) 4359 – 4369.

[12] Seungho Choi, Soonil Lee, and Ken Ha Koh, Hot filament effects on CVD of carbon nanotubes, Phys. Stat. Sol. (RRL) 1 (2007) 156-158.

[13] Z. P. Huang, J. W. Xu, Z. F. Ren, J. H. Wang, M. P. Siegal, and P. N. Provencio, Growth of highly oriented carbon nanotubes by plasma-enhanced hot filament chemical vapor deposition, Appl. Phys. Lett. 73 (1998) 3845-3848.

[14] H. Sato, Y. Hori, K. Hata, K. Seko, H. Nakahara, and Y. Saito, Effect of catalyst oxidation on the growth of carbon nanotubes by thermal chemical vapor deposition, J. Appl. Phys. 100 (2006) 104321-104325. https://doi.org/10.1063/1.2364381.

[15] Jimena Olivares, Teona Mirea, Barbara Diaz-Duran, Marta Clement, Mario DeMiguel-Ramos, Jesus Sangrador, Jose de Frutos, and Enrique Iborra, Growth of carbon nanotube forests on metallic thin films, Carbon 90 (2015) 9-15.

[16] L. Nilsson, O. Groening, C. Emmenegger, O. Kuettel, E. Schaller, L. Schlapbach, H. Kind, J. M. Bonard, and K. Kern, Appl. Phys. Lett. 76 (2000) 2071 - 2073. https://doi.org/10.1063/1.126258.

[17] Chi Li, Yan Zhang, Mark Mann, David Hasko, Wei Lei, Baoping Wang, Daping Chu, Didier. Pribat, Gehan A. J. Amaratunga, and William I. Milne, High emission current density, vertically aligned carbon nanotube mesh, field emitter array, Appl. Phys. Lett. 97 (2010) 113107 – 113110. https://doi.org/10.1063/1.3490651.