GROWTH OF CNT FORESTS ON TITANIUM SUBSTRATES: EFFECT OF CATALYST RATION AND HYDROGEN ON THE INCORPORATION OF NITROGEN INTO CARBON NANOTUBE STRUCTURE

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Abstract
For better electrical contacts of potential devices, growth of vertically aligned carbon nanotubes (CNT forests) directly onto conductive substrates is an emerging challenge. Here, we report a systematic study on the CCVD synthesis of carbon nanotube forests on titanium-based substrates. As a crucial issue, the effect of the presence of an insulating layer (alumina) on the growing forest was investigated. Other important parameters, such as the influence of water vapor or the Fe-Co catalyst ratio, and the incorporation of nitrogen into carbon nanotube were also studied during the synthesis. As-prepared CNT forests were characterized by various techniques: scanning and transmission electron microscopies, Raman spectroscopy, energy-dispersive X-ray spectroscopy, spectroscopic ellipsometry.

Introduction
In the past two decades, in the field of carbon nanotube (CNT) research important results have been achieved, which revealed that carbon nanotubes have extremely good electrical and mechanical properties. Vertically aligned carbon nanotubes (VACNT) which are often referred to as carbon nanotube forests in the literature (CNT forest), were synthesized for the first time in 1996 [1]. Their synthesis is a key issue therefore many efforts have been done to improve quality. Growing well-aligned carbon nanotube forests is a promising tool in order to finely tune features required [2]. Although, there is a growing understanding about the molecular-level mechanism of this so called “super-growth” method, still studying the influence of the synthesis conditions on the physicochemical properties of CNTs is still crucial, in order to reveal and tune the parameter space of the properties such as the orientation, the height, the density, and degree of graphitization. The catalyst layer can be deposited *via* various techniques. In 2007, Noda et al. [3] studied the effect of the presence of aluminum oxide on silicon substrate in relation to the synthesis of carbon nanotube forests. They have found that the intermediate oxide support on the silicon substrate was crucial to provide a strong interaction between the oxide layer and the catalyst layer. Here, we investigate the effect of aluminum oxide support on the growth of carbon nanotube forests over metallic titanium substrates as well as few parameters that influence the growth of carbon nanotube forests (ratio of catalyst, the effect of hydrogen, the incorporation of nitrogen).

Experimental
Catalyst Layer Production
Catalyst and oxide layers were prepared by PLD method. Catalyst and oxide target were made of metal oxides’ powder (Fe_2O_3, CoO and Al_2O_3) with a total weight of 1 g shaped into a 1 cm diameter pellet. The mechanical resistance was improved by heat treatment, which in this

case lasted 4 h at 500◦C in air. In order to provide reproducible adhering conditions onto the substrate, the titanium substrate was sequentially washed with distilled water, absolute ethanol, and acetone prior to catalyst layer deposition. For the layer deposition, laser pulses of a LLG TWINAMP ArF excimer laser (λ = 193 nm, pulse length: 18 ns, repetition rate: 10 Hz) with average fluence of 13 J/cm^2 were focused on the target pellets placed in front of the titanium substrate where the layer was formed. The target substrate distance was 3 cm. According to a previous thickness optimization [4], the catalyst layer thickness was set to be 5 nm proven by spectroscopic ellipsometry measurements (Woollam M-2000F).

CCVD Synthesis

For the carbon nanotube forest production, the CCVD synthesis method was used. The titanium sheets including the catalyst layers were cut into 4×4 mm small sheets, in order to fit the quartz boat, (diameter 20 mm). Experiments were carried out at 700°C and the reaction time was 30 min. During the synthesis, the carrier gas was nitrogen with a flow rate of 50 cm^3/min, the carbon source was ethylene with a flow rate of 70 cm^3/min, the reducing agent was hydrogen with a flow rate of 50 cm^3/min, while the system contained water vapor with a flow rate of 30 cm^3/min, which contributed to the growth of carbon nanotube forests, and the N-containing compound (TPA- tripropylamine) had a flow rate of 45 cm^3/min in some cases.
In the first step of the synthesis, the reactor was purged with nitrogen to exclude oxygen from the system (2 min). Then hydrogen gas was introduced into the reactor, to reduce the catalysts (5 min). Subsequently, ethylene and water vapor were added to the synthesis. When the reaction was finished, all gas flows were closed, except nitrogen gas, which remained in the system for an additional 5 min. After the reactor was removed from the oven, and it was cooled to room temperature; in the final step as-synthesized samples were removed from the reactor. “Blank” synthesis was also carried out with the elimination of carbon source ethylene (Figure 1.) [5].

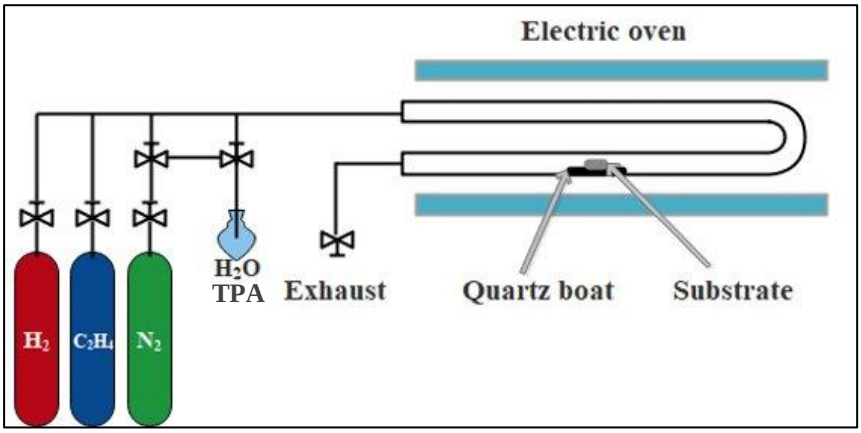

Figure 1. Schematic image of CCVD reactor.

Microscopic and Spectroscopic Investigations

Characterization of CNT Samples The orientation of the CNT forests was investigated by the means of Scanning Electron Microscopy (SEM), which type was Hitachi S-4700 Type II FE-SEM (5–15 keV). The diameters of the carbon nanotubes were examined by Transmission Electron Microscopy (TEM, Philips CM 10, 100 keV). The graphitic properties of CNT were analyzed by Raman Spectroscopy (Thermo Scientific DXR Raman microscope, excitation wavelength 532 nm).

Results and discussion

We successfully prepared carbon nanotube forests on titanium substrate both with and without Al_2O_3, and investigated the effects of water vapor and the incorporation of nitrogen-containing compounds in carbon nanotubes. Based on SEM images, the height of carbon nanotube forests have an outstanding value with water vapor, especially when the substrate was with Al_2O_3 layer. In those cases when no water vapor was present in the system, the height of the carbon nanotube forests was lower, when without alumina layer on the titanium substrate, the height of the carbon nanotube forests was only 5 µm, which is an extremely low height in therein research. As well as to the effect of hydrogen that the presence of the promoter plays an influential role on the height of carbon nanotube forests and in the incorporation of nitrogen, in the results can be achieved the lower height of carbon nanotube forests in the absence of hydrogen and suppress the incorporation of nitrogen into the carbon nanotubes.

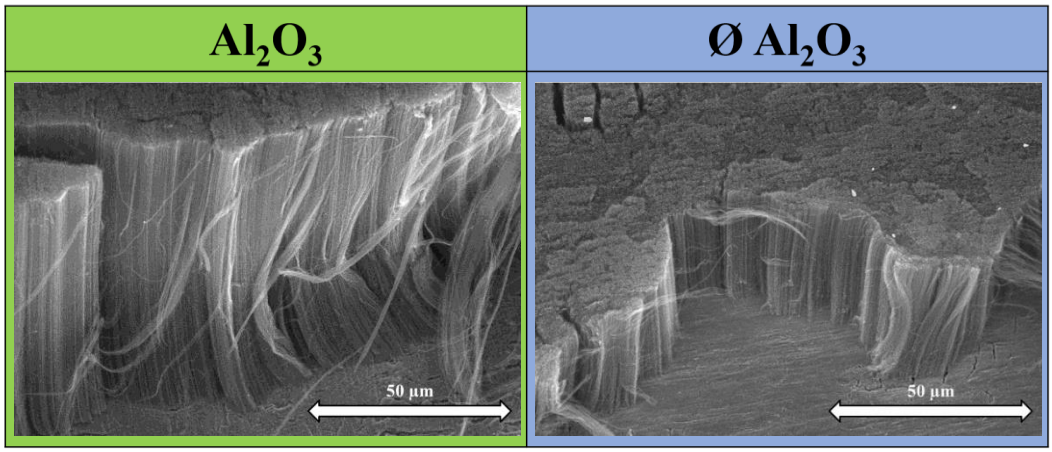

Figure 2. SEM images of CNT forests synthesized with Al_2O_3 oxide support and without Al_2O_3 oxide support

The catalyst morphology, of a sample with a layer thickness of 5 nm, was investigated right after the heat treatment. During this blank synthesis, the carbon source was not allowed into the system. From the SEM images, it can be observed, that the catalyst particles are separated when the oxide layer is deposited in advance onto the surface of the substrate and their average diameter is 27.5 ± 5.7 nm. However, when there was no aluminum oxide layer on the substrate, the catalyst particles were aggregated probably as a result of the different wetting properties of the oxide and the metal and their average diameter was 50.4 ± 11.6 nm.

TEM analysis was carried out to verify the quality of individual carbon nanotubes. TEM investigations revealed that fewer defects can be detected in the CNT walls when an oxide layer is also deposited on the titanium substrate. HR-TEM images revealed that the CNTs were typically consisted of 8–9 walls in average. The CNT with an increased number of walls showed much less graphitic features. The outer diameter of carbon nanotubes was between 12–13 nm for both samples. Based on the Raman spectra, only a small difference was observed, however, in the presence of Al_2O_3 the value of the I_G/I_D peaks fraction was: I_G/I_D = 1.18, while in the absence of Al_2O_3 it was IG/ID = 1.33.

We investigated the composition of different catalyst ratios to influence the height of carbon nanotube forests with and without Al_2O_3 layer.

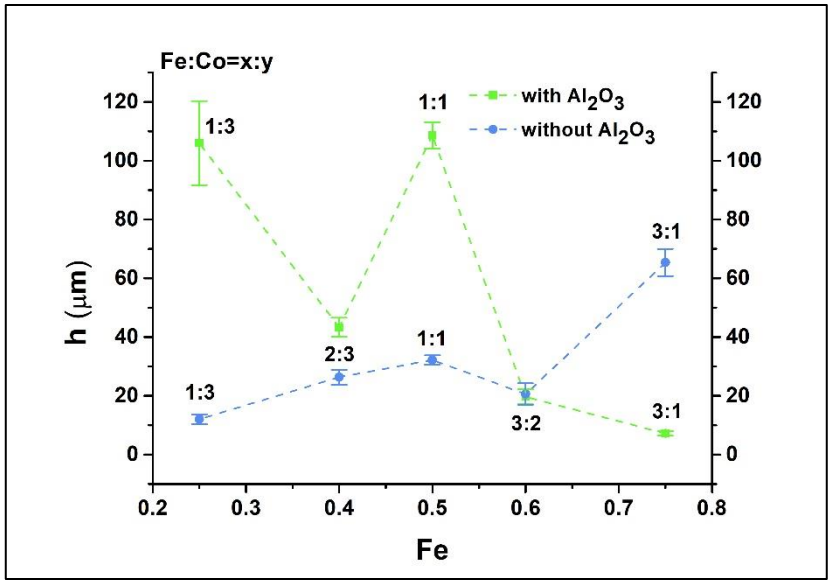

Figure 3. Heights of CNT forests with Al_2O_3 oxide support and without Al_2O_3 oxide support.

From the results of the two series, it was observed that in the presence of an insulating oxide layer on the surface of titanium substrate higher CNT forests were obtained. Interestingly, when the catalyst ratio was 2:3 or 3:2, the height of the CNT forests was relatively close in both cases, independently of the presence of the alumina layer. In our case when there was Al_2O_3 oxide support on the substrate, the highest CNT forest grew over the layers with 1:1 and 1:3 ratio as shown in Figure 3. In the second case when the substrate was applied without Al_2O_3 oxide layer, the maximum height of carbon nanotube forests was observed at the ratio of 3:1 as shown in Figure 3 and practically the height increases linearly with iron content.

Conclusion

In conclusion, certain parameters during both catalyst preparation procedure and CCVD synthesis can strongly affect the growth of vertically aligned carbon nanotubes. Applying titanium plates as a substrate it was found that the presence of an alumina layer on the surface significantly modifies the morphology of the catalyst layer (before reaction), thus influencing the CNT forest growth. One could expect that titanium as a metallic substrate dissolves reduced Fe-Co nanoparticles during preliminary hydrogenation and in this way completely inhibits carbon deposition. However, in this study, titanium proved to show a different feature. Nevertheless, it was attested that the insulating layer plays a significant role in CNT forest formation: both the height and the quality of CNT forest depended on the initial structure of the catalyst layer. It was also pointed out that water vapor in the gas feed during CCVD considerably affects the same parameters of the final product and that the presence of hydrogen in the system affects the incorporation of nitrogen into the carbon nanotubes. Structural characterization revealed important differences in CNT forests grown with or without alumina layer. These minor differences can be a result of many parameters such as graphitization of the CNTs, presence of alumina layer, density of CNT forest, fabrication conditions, etc. Therefore, we could postulate that the alumina layer does not play an important role as a current blocking layer.

Acknowledgements
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