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Research Article

Investigation and Optimization of Temperature Dependent Parameters for Growing Millimeter-Long Vertically Aligned Carbon Nanotubes

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Abstract

This study aimed to investigate effects of temperature dependent parameters on vertically aligned carbon nanotube (VACNT) forest height such as catalyst treatment temperature and growth temperature and optimize these parameters to grow long VACNT forests. These growth parameters were examined and optimized on samples including three different thicknesses of Fe catalyst layers which catalyze VACNT growth. Heights of VACNT forests grown on different Fe catalyst layers linearly decreased at various rates with the increment of the catalyst treatment temperature from 500 ℃ to 800 ℃. Moreover, optimum growth temperature to grow long VACNTs was found to be independent from Fe catalyst layer thickness while their height distributions showed variations. As a result of optimization of these parameters, we have found that it is possible to grow millimeter long VACNT forests from all three Fe catalyst layers with substantially low gas flows in 30 min growth. Raman spectroscopy approved that disorder of grown VACNTs is very low. Use of low gas feedstock, achieved in this study, ensures green and economic production of VACNTs.

Keywords: Carbon Nanotube, Chemical Vapor Deposition

Milimetre Uzunluğunda Dikey Hizalanmış Karbon Nanotüpler Büyütmek için Sıcaklığa Bağlı Parametrelerin İncelenmesi ve Optimize Edilmesi

Öz

Bu çalışma katalizör hazırlama sıcaklığı ve büyütme sıcaklığı gibi sıcaklığa bağlı parametrelerin, dikey hizalanmış karbon nanotüp (DHKNT) yığınlarının boyları üzerine olan etkilerini araştırmayı ve uzun DHKNT'ler büyütmek için bu parametreleri optimize etmeyi amaçlamıştır. Bu parametreler, DHKNT büyümesine aracılık eden Fe katalizör tabakasının üç farklı kalınlığını içeren örnekler üzerinde test edilip optimize edilmiştir. Farklı kalınlıklardaki Fe katalizör tabakalarından büyüyen DHKNT yığınlarının boyları, katalizör hazırlama sıcaklığının 500 ℃'den 800 ℃'ye arttırılması ile farklı hızlarda doğrusal bir azalma eğilimi göstermişlerdir. Diğer taraftan uzun DHKNT büyütmek için gerekli optimum sıcaklığın Fe katalizör tabakasının kalınlığından bağımsız olduğu fakat farklı kalınlıklardaki Fe katalizör tabakalarından büyüyen DHKNT yığınlarının yükseklik dağılımlarının değişiklikler gösterdiği bulunmuştur. Bu parametrelerin optimizasyonu sonucunda oldukça düşük gaz oranları kullanılarak 30 dakikada üç farklı kalınlıktaki Fe katalizör tabakalardan milimetre uzunluğunda DHKNT yığınlarının büyütülmesinin mümkün olduğunu bulduk. Raman spektroskopisi, büyütülen DHKNT'lerin düzensizliğinin oldukça düşük olduğunu göstermiştir. Bu çalışmada ulaşılan düşük miktardaki gaz kullanımı, çevreci ve ekonomik DHKNT üretimi imkanı sağlamaktadır.

Anahtar Kelimeler: Karbon Nanotüp, Kimyasal Buhar Çökeltme

1. Introduction

Carbon nanotubes (CNTs) exhibit multi-functional material properties due to their unique structural, electrical, mechanical and thermal capabilities (Jorio et. al., 2007). For more than two decades, they have been investigated by many researchers and used as the building material in broad range of applications such as nanoelectronics (Pan et. al., 2015; Che et.al., 2014), sensors (Gül et. al., 2016; Jacobs et.al., 2010), energy storage (Corso et. al., 2014; Lee et. al., 2010), composites (Shokrieh et. al., 2010) and many others. CNT growth studies still go on in order to achieve low cost, eco-friendly, high quality, controllable and scalable CNT production (Wang et. al., 2010; Liu et. al., 2017).

Their integration to technology has been employed in many fields and this requires significant amount of CNT production. Estimated amount of commercial production of CNTs at 2011, not including research purposed productions, was calculated as more than 4.5 kiloton/year (De Volder et. al., 2013). This amount of production needs excessive carbon feedstock and it causes exhausting high carbon waste products that threat the environment and living creatures. On the other hand, high carbon feedstock necessity negatively effects wide usability of CNT in technology in a cost-effective manner. However, it is possible to reduce used carbon feedstock amount by investigating optimum growth parameters that improves CNT growth quality.

Chemical vapor deposition (CVD) is the most scalable and controllable technique in CNT growth that allows location and diameter controls of CNTs (Su et. al., 2000). CNTs are grown by CVD technique on a metal coated oxide layer. Typically, a thin layer of a transition metal such as Fe, Ni, Co, Pd, Pt, Ag, Au is used as catalyst nanoparticles for CNT growth (Huh et. al., 2005; Takagi et. al., 2006). For vertically aligned CNTs (VACNTs) growth, additional Al_2O_3 layer as a support to catalyst nanoparticles is usually preferred (Mi et. al., 2007). Al_2O_3 support layer and a transition metal layer are deposited on Si/SiO_2 by e-beam, thermal evaporator or magnetron sputter. VACNT growth occurs in the presence of a carbon source gas like ethylene, acetylene, methane at a temperature range about 500-1000 ℃ in a CVD furnace.

CVD grown VACNTs quality depends on some independent and interdependent parameters such as catalyst type, catalyst layer thickness, catalyst treatment, growth temperature, growth duration and gas flow rates. There is no standard recipe that gives the best result for VACNT. On the other hand, VACNT growth results exhibit variation from one CVD system to another even same parameters are used. However, meticulous optimization of these parameters for each CVD system can result with high density, well aligned, mm-long CNT forest.

Herein we investigated some growth parameters for optimization of VACNT growth in our CVD system in order to achieve high quality VACNTs. We have studied on temperature dependent parameters such as the catalyst treatment temperature and the growth temperature. We prepared samples coated with three different thicknesses of Fe catalyst layers, 1nm, 3nm, 5nm, and use them in all experiments side by side in order to find out the effect of these parameters on different catalyst layer thicknesses. As a result of optimization of these parameters we have found that we are able to grow mm long VACNT forests from all Fe layers with substantially low gas flows in 30 min growth.

Use of low carbon feedstock provides an advantage since it ensures green and economic production of VACNTs. Moreover, the optimization of temperature parameters studied in this work may provide significant input to VACNT growth researches.

2. Materials and Methods

One side polished (100) Si wafers coated with 300 nm SiO_2 layer on top are used for VACNT growth experiments. Si/SiO_2 wafers are first cleaned chemically by acetone, isopropyl alcohol (IPA) and deionized (DI) water, then treated thermally at 130 °C for 10 minute. After the cleaning, catalyst layer deposition on Si/SiO_2 wafers is performed with e-beam evaporation (Vaksis E-Beam Evaporator). High purity Al_2O_3 (99.99%) and Fe (99.9%) pellets are used as evaporation targets. First, 10 nm Al_2O_3 as a support layer is deposited on SiO_2 with a rate 0.3-0.5 nm/s, then Fe as a catalyst layer is deposited on Al_2O_3 with a rate 0.1-0.2 nm/s in low pressure chamber, 10^{-6} Torr. Thicknesses of Fe catalyst layers for different wafers are established as 1 nm, 3 nm and 5 nm. Wafers are then diced into pieces of 7x7 mm in order to be used as substrates in different VACNT growth experiments.

VACNT growth is carried out in a small, horizontal quartz tube furnace (22 mm inner diameter and 300 mm hot zone length) at atmospheric pressure (Figure 1a). Gas flow rates are controlled by flow controllers that are managed with a custom-built computer program. High purity Ar (99.99%), H_2 (99.99%) and C_2H_4 (99.95%) gases are used in experiments. Substrates loaded on a quartz boat are located at the cold zone of the furnace, then the open end of the quartz tube is closed. The quartz tube is flushed with 300 standard cubic centimeter per minute (sccm) Ar for 5 min before ramping temperature up. Temperature of the furnace is ramped up to catalyst treatment temperature with the rate of 100 °C/min in the presence of 300 sccm Ar flow.

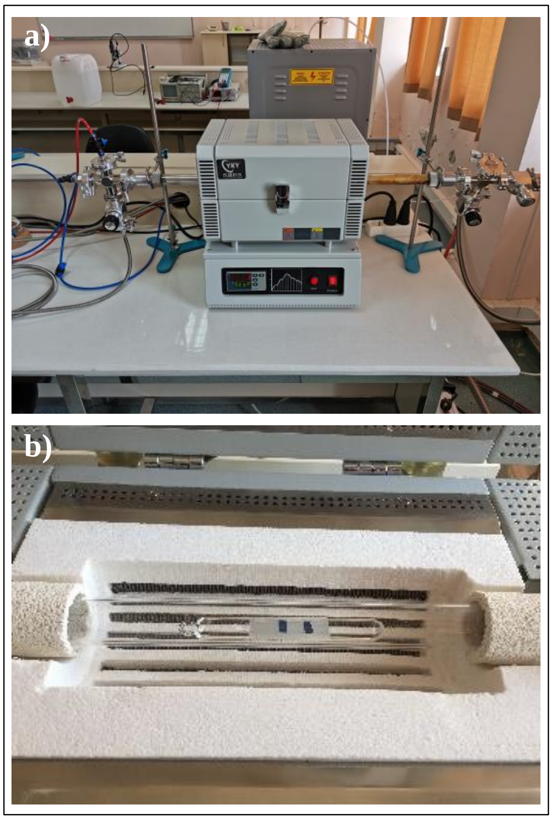

Figure 1. (a) CVD furnace. **(b)** The view of the quartz boat loaded with substrates in the hot zone of the CVD furnace.

The quartz boat loaded with substrates are inserted into the hot zone with the help of a stainless bar (Figure 1b). The catalysts are treated in 40/10 sccm H_2/Ar for 5 min at various temperatures for the catalyst treatment temperature experiments otherwise at a constant treatment temperature. After the catalyst treatment, the furnace temperature is ramped up to the growth temperature in the presence of 50 sccm Ar flow. The growth temperature is set to 800 °C except growth temperature experiments which temperature varies about 720-840 °C. VACNTs are grown in 10/40/10 sccm of C_2H_4/H_2/Ar in 30 min. Substrates are cooled down rapidly by opening the cover of the furnace while flowing 300 sccm Ar. After the fast cooling, the furnace is flushed with 300 sccm Ar for 5 min before opening the quartz tube for taking substrates out.

Heights of VACNT forests are measured in scanning electron microscope (SEM) at 5 kV (Nova NanoSEM). VACNTs are characterized by Raman spectroscopy using 532 nm laser (Renishaw inVia InSpect) in order to determine their crystal structures.

3. Results and Discussions

Figure 2 shows representative SEM images of VACNT forests that were grown with different growth parameters. They clearly represent the variety of VACNT forests heights. Forests heights in our CVD system for typical 30 min growth vary from 10 μm to 1.6 mm depending on VACNT growth parameters. Average growth rates of VACNTs for the highest and the lowest forests are 53 μm/min and 0.33 μm/min, respectively. The substantial difference between the two growth rates is an indicator for understanding the importance of determining the optimum growth parameters for a CVD system in order to achieve the efficient growth.

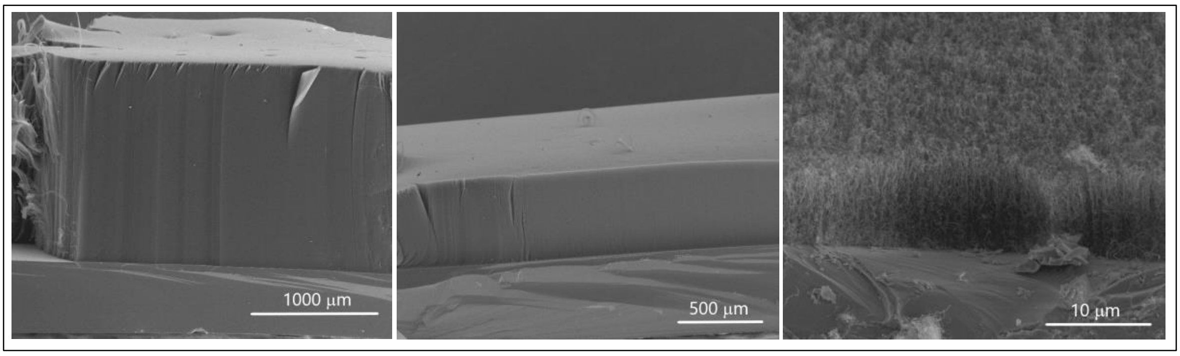

Figure 2. SEM images of VACNT forests grown with various growth parameters.

Treatment of Fe catalyst layer in the presence of H_2 gas is a crucial step for Fe nanocluster formation before VACNT growth (Sakurai et. al. 2012). One factor that is responsible for Fe nanocluster formation to grow long/short VACNTs is the catalyst treatment temperature (Zhan et. al. 2011). Figure 3 shows catalyst treatment temperature dependence of VACNT forests heights that were grown on different Fe thicknesses at 800 °C. All catalyst treatments were carried out for 5 min. VACNT forests grown on each Fe thickness showed same height trend that decreases with increasing catalyst treatment temperature. A linear decrease on height of VACNT forests have been observed for all.

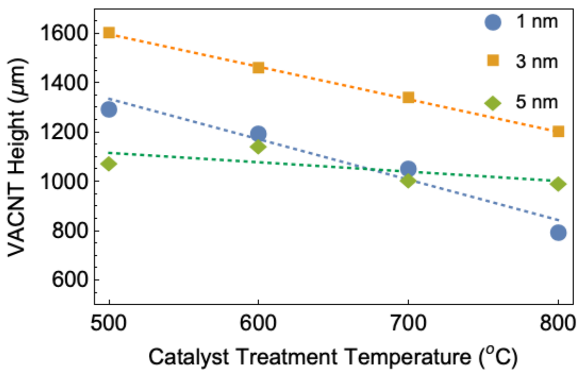

Figure 3. The variation of VACNT forests heights with catalyst treatment temperature. Three plots correspond to heights of VACNT forests that grown on 1nm, 3nm and 5 nm Fe catalyst layers. Dashed lines are linear fits to each data set.

The equation that describes the height decreases of VACNT forests with increasing catalyst treatment temperature could be expressed by

$$H(T) = h_0 - r(T - 500), \qquad (1)$$

where H is the height of the forest that is the function of the catalyst treatment temperature T which varies in the range $500 \leq T \leq 800$, h_0 is the theoretical height at $T = 500$ °C, r is the height reduction rate. The equation indicates linear decreases of VACNT forests heights with respect to catalyst treatment temperature. Table 1 shows the values of fitting parameters in the Equation 1.

Table 1. Fitting parameters on the equation 1 for VACNT forests grown on 1nm, 3nm and 5nm Fe catalyst layers.

	1 nm Fe	3 nm Fe	5 nm Fe
h_0 (μm)	1308.00	1598.00	1117.00
r (μm/°C)	1.52	1.32	0.38
$H(800)$	844.00	1202.00	1003.00

The height of VACNT forest, grown on 1 nm Fe, decreased from 1300 μm to 800 μm with the rate of 1.64 μm/°C. The reduction of the forest height, grown on 3 nm Fe, occurred from 1600 μm to 1200 μm with a slightly slower rate 1.32 μm/°C. On the other hand, the height of VACNT forest, grown on 5 nm Fe, decreased only from 1080 μm to 1000 μm with a very slow rate of 0.38 μm/°C. According to the height reduction rates on Table 1, while the thickness of the catalyst layer increases, the degree of variation on VACNT forests heights with the catalyst treatment temperature become smaller. The optimum catalyst treatment temperature, in terms of VACNT forest height, was found 500 °C for 1nm and 3 nm Fe catalyst layers and 600 °C for 5nm Fe catalyst layers in Figure 3.

VACNT growth temperature is another parameter that effects VACNT forest height (Wirth et. al. 2009). Growing VACNT forest with varying heights at different temperatures in a broad range is possible. In Figure 4, height distributions of VACNT forests grown on different Fe catalyst thicknesses in a temperature range from 720 °C to 840 °C are seen. Temperature dependent height distribution of VACNT forests exhibited gaussian-like behavior. Regardless of the catalyst thickness, the optimum growth temperature to grow longer VACNT forest was found as 800 °C. Moreover, we observed sharp decreases at the forests heights around 800 °C indicating that even a small temperature change plays an important role on the forest height.

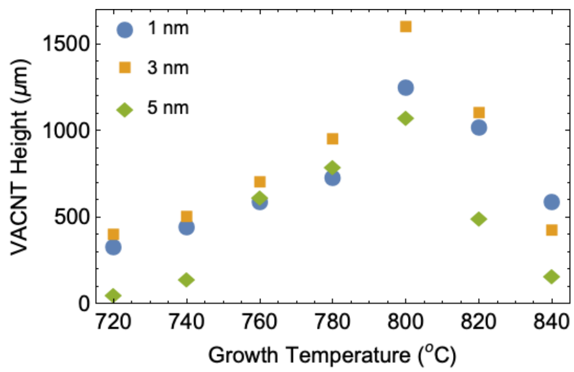

Figure 4. Temperature dependent height distributions of VACNT forests grown on 1 nm, 3nm and 5 nm Fe catalyst layers.

Height distributions of VACNT forests grown on 1 nm and 3 nm Fe catalyst layers presented very similar behavior in whole range. On the other hand, VACNT forests grown on 5 nm Fe catalyst layer were more effected from temperature changes, especially at low and high temperatures and it resulted with very short forests grow. According to Figure 4, 3 nm Fe catalyst thickness resulted with longer VACNT forest growth comparing to 1 nm and 5 nm thicknesses in 30 min growth.

We have determined the crystallinity of VACNTs by Raman spectroscopy. Raman spectrum of VACNTs grown on various catalyst thicknesses at 820 °C were shown in Figure 5. In general, the tangential mode (*G*-band) corresponds to existence of crystalline graphitic carbon in CNTs while the disorder mode (*D*-band) indicates disorder in the structure. The *G*-band and the *D*-band of multi walled CNTs (MWCNTs) are seen at ~1580-1600 cm^{-1} and ~1330-1350 cm^{-1}, respectively. The ratio of the intensity of the D-band peak (I_D) to the intensity of the G-band peak (I_G) is an indicator of the amount of CNT disorders (Dresselhaus et. al., 2005).

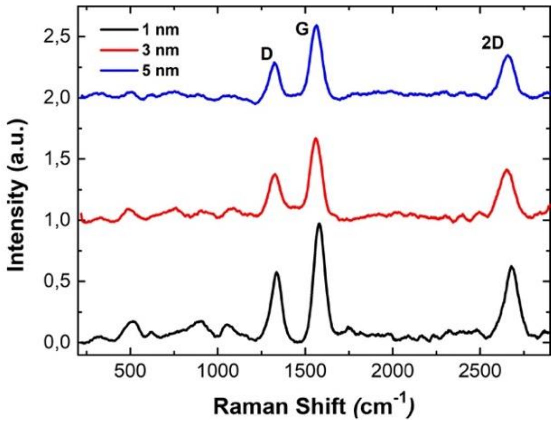

Figure 5. Raman spectrum of VACNTs grown on 1 nm (top), 3nm (middle) and 5 nm (bottom) Fe catalyst layers.

In our study, the *G*-band peak of VACNTs grown on all three Fe thicknesses are located at 1571-1584 cm^{-1} indicating the presence of MWCNTs in forests (Table 2). The *D*-band peaks arising at 1328-1341 cm^{-1} show the existence of disorders which is usual in VACNTs. However, I_D/I_G ratios for all VACNTs are reasonably smaller than 1. This means that disorder of VACNTs are less and their crystallinity is considerably good. Disorder amount of VACNT slightly decreases while Fe catalyst layer thickness increases.

Table 2. Raman Parameters for VACNTs grown on 1nm, 3nm and 5nm Fe catalyst layers.

	1 nm Fe	3 nm Fe	5 nm Fe
D (cm^{-1})	1341.03	1332.40	1328.07
G (cm^{-1})	1583.86	1567.03	1571.24
G'(cm^{-1})	2683.90	2658.00	2665.41
I_D/I_G	0.5943	0.5282	0.4882

4. Conclusions

In summary, we investigated effects of catalyst treatment temperature and growth temperature on VACNT forest height and found optimum temperature values for achieving maximum height. Optimum growth temperature for all Fe catalyst layer thicknesses, we tested, was found 800 °C. Besides, optimum catalyst treatment temperature was found to be lower than the growth temperature. Height of VACNT forest linearly decreased with the increment of the catalyst treatment temperature. Optimization of temperature dependent parameters yielded mm long VACNT forests grow for all Fe catalyst layer thicknesses, we used.

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