Synthesis of Carbon Nano Tubes on Silicon Substrates Using Alcohol Catalytic Chemical Vapor Deposition

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ABSTRACT

The technique used for synthesizing large quantity carbon nanotubes (CNTs) directly on the surface of silicon substrates has been developed by means of the alcohol catalyst chemical vapor deposition ACCVD method using ethanol. The proposed method adopts an easy and costless liquid-based dip-coat approach for mounting the catalytic metals on the substrates. Reasonable quality formation of catalyst preparation was found at 5 min of dipping the substrate into cobalt acetate solution and withdrawing at speed of 4 cm/min followed by heat treatment at 400°C. Cobalt acetate catalyst on silicon substrates were analyzed using an atomic force microscopy (AFM) and scanning electron microscopy (SEM). The substrate surface is blackened with a layer of CNTs after the ACCVD at an optimum condition. The grown CNTs were analyzed using transmission electron microscopy TEM, SEM, XRD, UV/Vis-NIR spectroscopy and photoacoustic (PA) measurements of thermal parameters. Large quantities of single and multi walled carbon nanotubes were grown at a growth time of 50 min and growth temperatures of 800°C and 900°C. UV-Vis/NIR spectroscopy detected two absorption peaks at 0.78 and 1.35 eV and optical energy gap (E_{opt}) of 1.16 eV for CNTs grown at 800°C. The PA measurements of thermal parameters detected maximum values of thermal diffusivity, effusivity and conductivity for those grown at 800°C.

Keywords: CNTs, ACCVD, Dip Coating, Synthesis, Catalysts, Optical, Thermal

1. Introduction

Carbon nanotubes (CNTs) have recently gained great interest in science and industry due to their highly considerable promises in enabling the future nano-structured materials with novel properties [1,2]. In this respect, CNTs with their huge aspect ratio in combination with high strength and stiffness have become potential reinforcing constituents to get common engineering polymers into multi-functional composites with superior properties such as conductive polymers with improved mechanical performance [1,3]. Despite many reported studies in the literature, the achievement of the desired improvement via CNTs in final properties of their polymer based composites has not been successfully realized so far [4-6].

Carbon nano tubes have been drawing increasing attention [7,8] since their discovery [9]. CNTs is divided into single walled (SWCNTs), double walled (DWCNTs) and multi walled (MWCNTs). Various synthetic methods have been developed for the production of CNTs, including arc-discharge [10-12], laser ablation [13], pyrolysis [14], plasma enhanced [15] and thermal chemical vapor deposition (CVD) [16]. In the last few years, CVD has been the preferred method among different methods because of its potential advantage to produce a large amount of CNTs growing directly on a desired substrate with high purity, large yield, and controlled alignment, whereas the nano tubes must be collected separately in the other growth techniques. Depending on the final application, thermal CVD could be even more desirable than plasma CVD because thermal CVD processes are more economical, suitable for large-area, irregular-shaped substrates, and multiple-substrate coatings [17,18]. Additionally, using CVD one can control the diameter [18,19], length and orientation [19,20] of the nano tubes. Various CVD methods are now available for SWCNTs synthesis, including disproportionation of CO [21-23], high pressure catalytic decomposition of carbon monoxide (HiPCO)
the recently introduced alcohol catalytic chemical vapor deposition (ACCVD) [26-32]. In the ACCVD method developed by Maruyama et al. [26], bimetallic Fe–Co nano-particles impregnated into zeolite supports are used as the catalysts and alcohol vapor is used as the carbon source to obtain SWCNTs with high purity at 800°C. The high purity is attributed to OH radicals associated with alcohols, which effectively removes the amorphous carbon during growth. This method is economical and offers advantages such as low synthesis temperature, simplicity and high yield as determined by a thermal gravimetric analyzer (TGA) [28]. The ACCVD method was also used to synthesize SWCNTs on substrates such as quartz, silicon [28,30] and mesoporous silica [29]. Dip coating was utilized for loading catalyst particles onto the substrates, and either randomly [28] or vertically aligned [30,31] SWCNTs were obtained. The vertically aligned SWCNTs were obtained by utilizing a good background vacuum and low leak conditions. In addition to the work of Maruyama et al., alcohol vapor has also been shown to be an effective carbon source for synthesis of SWCNTs by other groups [33-35].

In this work, we will report on the growth of CNTs using the ACCVD method. We will perform a parametric study of various factors influencing both the preparation of catalyst and the growth of carbon nanotubes. Specifically, we will investigate the effect of the time of immersion of Si substrates in cobalt acetate solution as well as the temperature of heat treatment for the prepared catalysts. The effect of growth temperature on the characteristics of grown CNTs will also be investigated. Analysis of the prepared CNTs will be done using SEM, TEM, UV-Vis/NIR spectroscopy. Thermal parameters of the grown CNTs will also be studied.

2. Experimental Details

2.1. Preparation of Catalyst

Metal acetate solution was prepared first by dissolving cobalt acetate (CH₃COOH)₂Co·4H₂O (99.999%, Sigma-Aldrich) into ethanol (typically 42 mg of cobalt acetate in 10 ml of ethanol) so that the concentration of each metallic species was 0.01 wt% with stirring for 10 min followed by sonication for 2 h at room temperature. The choice of Co catalyst because of its better performance over the others, at least, in the tested range of metallic concentrations and CVD conditions [29].

For a substrate, we employed p-type Si wafer with (100) surface polished at one surface (University Wafers, USA) and a thickness of 0.5 mm. The substrate was cut into a strip of about 10 × 25 mm². The substrate was cleaned by consecutive acetone sonication for 5 min, washed with DI water and blown with dry nitrogen.

The dip coating method was applied to substrates. The substrate was held by a small clip with a stabilizing weight and a nylon fishing line. The substrate piece was then submerged vertically into a prepared metallic acetate solution for different times (typically 5 and 10 min), leaving upper 5 mm of it above the solution level to prevent the clip from contacting the solution. This piece was then drawn up from the solution at a constant speed of 4 cm/min. The surface of the substrate was rapidly dried at several millimeters above the liquid contact level as soon as it was removed from the solution. Right after this process, the piece was placed in a furnace and maintained at 400°C or 500°C for 5 or 10 min.

2.2. Growth of Carbon Nano Tubes

CNTs were grown via the alcohol catalytic chemical vapor deposition (ACCVD) technique using a 50 cm long ceramic tube furnace and diameter of 12 cm as shown schematically in Figure 1. The reasons behind the choice of this method are low cost and one produces a large quantity of CNTs [36]. The growth process followed the following procedure. Cobalt acetate supported catalyst was placed into alumina combustion boat; whereas a 10° inclined graphite stage was used to support the substrates and the group was then placed at the center of the tube furnace. The tube was evacuated to 150 mTorr, and samples were heated to the desired reaction temperature under 250 sccm of flowing argon. Once the growth temperature was reached (depending on the growth temperature), samples were held at that temperature for 5 min. The argon was then shut off and the tube was evacuated before the introduction of alcohol vapor. The alcohol vapor (ethanol) was then transferred into the tube furnace to achieve a pressure of 5 - 10 Torr. The alcohol flow rate in the growth chamber was controlled by controlling the alcohol bath temperature. After growth, the alcohol vapor was evacuated, argon was introduced again and the reaction tube was cooled to room temperature. CNT growth time was kept constant at 50 min unless otherwise stated.

2.3. Characterization of Catalysts and Carbon Nano Tubes

2.3.1. AFM, SEM, TEM and XRD

Surface analysis was performed using a Pico scan Agilent AFM contact mode in order to confirm the presence of nano particles catalysis that distributed above the Si substrate surface.

SEM studies were performed on a JSM-6380 high resolution scanning electron microscope operated at 20 kV in KSU, Saudi Arabia. Furthermore, nanotubes grown in powder form were sonicated in methanol and placed onto holey/lacey carbon coated copper grids for
Figure 1. Schematic presentation of the apparatus used in the growth of CNT.

TEM (Model 1011 JEM at 100 KV KSU, Saudi Arabia) observations to confirm both their existence and morphology.

The phase purity of the samples is examined using X-ray diffractometer with Cu-Kα radiation, 40 mA and 45 KV.

2.3.2. Optical Measurements

The absorption spectra of the prepared CNTs were measured using a scanning double beam UV-Vis/NIR spectrophotometer (Shimadzu, Model 1601) in the wavelength range 190 - 3000 nm at room temperature. The absorbance “A” was calculated according to the Beer-Lambert Law equation:

\[ A = \log_{10}\left(\frac{I}{I_0}\right) \]  

where, \( I \) is the transmission intensity through the sample and \( I_0 \) is the intensity through the air gap as a reference. The absorption spectra are presented as the absorbance versus wave length (nm) and energy (eV). The absorption coefficient \( \alpha \) of the samples composite was calculated from the optical absorption spectrum using the relation:

\[ \alpha(\nu) = 2.303 \frac{A}{d} \]  

where \( d \) is the sample thickness in cm and \( A \) is the absorbance [37-39].

2.3.3. Photoacoustic Measurements (PA)

A schematic diagram of the PA experimental set-up is presented in Figure 2. The PA measurements were carried out by Gas-microphone detection method. A xenon arc lamp was used as the light source. A monochromatic light beam at a fixed wavelength was obtained by passing the light through a monochromator. The light was modulated with a mechanical chopper and focused on the surface of a sample placed inside a sealed PA cell. The light absorbed by the sample is converted into heat by non-radiative relaxation processes and results in pressure fluctuations in the air inside the cell. The amplitude of the detected signal (by the microphone enclosed in the PA cell) as a function of modulation frequency is recorded using a dual channel digital lock-in amplifier (SR830). Sample holder was filled of samples (in the powder form), then entered into the PA chamber. The overall thickness of the sample is determined by the holder depth. For thermal effusivity measurements, the reference sample was Si wafer of known effusivity (1.5 Ws^{1/2}/cm²K).

3. Results and Discussions

3.1. Optimization of Catalyst Composition

Catalysts were prepared at different conditions to achieve the smallest available dimensions of particles on the substrate. The morphology of the substrate surface is very important to understand the particles (dispersed phase) distribution because it is the most important aspect which governs the growth of CNTs. SEM analysis of the substrates allows for the observation of a peculiar experimental feature. Figures 3(a) and (b) show the SEM micrographs of two substrates immersed in cobalt acetate solution for 10 min and then transferred to a box furnace and heated in air to 500°C and 400°C, respectively. The dispersed morphology could be witnessed by the figures. The cobalt particles are homogeneous and uniformly distributed over the surface of the substrates. The particles formed have approximately a spherical shape. The average minimum diameters of these particles for both conditions are 68 and 38 nm for catalysts heated at 500°C and 400°C respectively. On the other hand, particles formed on substrates with 5 min immersion in cobalt acetate, withdrawn at 4 cm/min and heated at 400°C have average minimum diameter of 9 nm as shown in Figure 3(c). The resolution of the used SEM is not high enough.
to show the detailed features of the surfaces, accordingly AFM is used to follow up more details.

Figures 4 and 5 illustrate the AFM three and two dimensional topography of catalysts prepared at temperatures 500°C, 400°C after immersion in cobalt acetate solution for 10 min and 400°C after immersion in the solution for 5 min only. These scans are acquired at 2 μm except for figures 4(c) and 5(c), which acquired at 0.5 μm. The scans are done in air at 25°C and scan rate of 1 Hz. It appears from Figures 4(a-c) that the surfaces are rough with two different types of small and large dispersed particles. Additionally, narrow features are present along the edges of the large particles of Figure 4(a). The height of these features is about 96 nm. In case of Figures 4(b) and 4(c) these features have heights of 106 and 13 nm, respectively. Fine detailed particles are, also present in Figure 4(c). Figures 6 and 7 show the section analysis of these substrates. Figure 6 detects maximum heights (z-direction) of 108, 35.5, and 4 nm for the particles formed on substrates thermally treated at 500°C with immersion time 10 min, 500°C with immersion time 10 min and 400°C with immersion time of 5 min, respectively. The average length (y-direction) of these particles are found to equal 114, 42, and 4.5 nm for same substrates as shown in Figure 7.

Statistical parameters of the particles dispersed on these different substrates prepared at different conditions are listed in Table 1. It is clear that the minimum particles parameters appear for substrates immersed in cobalt acetate solution for 5 min and then heated in air up to 400°C.

3.2. Growth of Carbon Nano Tubes

In ACCVD method for growing CNTs there are many factors affect the growth namely, growth time, carbon
Figure 5. Two dimensional images of catalysts prepared at (a) 500°C after immersion in cobalt acetate solution for 10 min, (b) 400°C after immersion in cobalt acetate solution for 10 min and (c) 400°C after immersion in cobalt acetate solution for 5 min.

Figure 6. 051 (z-direction) of the particles formed prepared at (a) 500°C after immersion in cobalt acetate solution for 10 min, (b) 400°C after immersion in cobalt acetate solution for 10 min and (c) 400°C after immersion in cobalt acetate solution for 5 min.

Figure 7. Lengths distribution (y-direction) of the particles formed prepared at (a) 500°C after immersion in cobalt acetate solution for 10 min, (b) 400°C after immersion in cobalt acetate solution for 10 min and (c) 400°C after immersion in cobalt acetate solution for 5 min.
source and growth temperature [36]. The change in alcohol flow rate does not affect the properties of grown CNTs [36]. In this work, the growth time is fixed at 50 min and the carbon source used is ethanol and its flow rate is fixed by fixing the temperature of the hot plate used to heat it. The growth temperature is changed at 400°C, 500°C, 700°C, 800°C and 900°C. SEM images of the nano tubes grown on cobalt acetate substrate at these temperatures are shown in Figures 8(a)–(e). At temperatures 400°C and 500°C, carbon appears to be a nano

Table 1. Statistical parameters for catalysts prepared at different conditions.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Substrate prepared at 10 min and heated to 500°C</th>
<th>Substrate prepared at 10 min and heated to 400°C</th>
<th>Substrate prepared at 5 min and heated to 400°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average value (nm)</td>
<td>27.38</td>
<td>8.40</td>
<td>2.24</td>
</tr>
<tr>
<td>Maximum (nm)</td>
<td>92.59</td>
<td>110.8</td>
<td>12.53</td>
</tr>
<tr>
<td>Median (nm)</td>
<td>26.43</td>
<td>5.8</td>
<td>1.98</td>
</tr>
<tr>
<td>Ra (nm)</td>
<td>6.08</td>
<td>4.8</td>
<td>0.64</td>
</tr>
<tr>
<td>Rms (nm)</td>
<td>8.82</td>
<td>9.0</td>
<td>1.04</td>
</tr>
</tbody>
</table>

Figure 8. SEM images of CNT grown on cobalt acetate catalyst on Si substrate at (a) 400°C, (b) 500°C, (c) 700°C, (d) 800°C and (e) 900°C.
powder of particle size ranging from 20 to 58.5 nm, respectively. At a higher temperature of 700°C, multiwalled carbon nano tubes with outer diameters ranging from approximately 12 to 37 nm appear beside the carbon nano powder as shown in Figure 9(a). On the other hand, the grown nanotubes at °C at same growth time appear to be mainly bundles of single walled carbon nanotubes with an average diameter of 1.6 nm as shown in Figure 9(b). At a growth temperature of 900°C the majority of grown nanotubes are multiwalled besides a little of single walled carbon nanotubes bundles as shown in Figure 9(c).

3.3. XRD Analysis

Figure 10 shows the XRD pattern for as prepared CNTs at temperatures (a) 800°C and (b) 900°C, respectively. The patterns confirm that the powders prepared by using ACCVD are CNTs with (002), (101), and (004) orientations [40-42]. The positions of these orientations are slightly shifted. The values of 2θ for these planes at 800°C are 26.097°, 44.783° and 52.013°, respectively, while they become 26.364°, 44.654° and 52.135°, respectively, when the growth temperature equal 900°C. The d-spacing of these planes are 3.425, 2.024 and 1.757 Å, respectively for CNTs formed at 800°C while for those prepared at 900°C the d-spacing values are 3.381, 2.029 and 1.753 Å respectively. The XRD of SWCNTs is characterized by a small relative intensity of the peak located at 2θ equal 26.097° [31].

Figure 9. TEM images of CNTs grown on cobalt acetate catalyst on Si substrate at (a) 700°C, (b) 800°C, (c) 900°C.
Figure 10. XRD patterns for CNTs grown at (a) 800°C and (b) 900°C.

3.4. Uv-Vis/NIR Spectroscopy

Jeong, M. S. and Byeon, C. C. [43] reported that the absorption spectrum of SWCNTs mainly consists of three absorption peaks. The first one is at around 0.8 eV (S11) and the second is at around 1.2 eV (S22) while the third one (M11) is at around 1.75 eV. The first two peaks corresponding to absorption characteristics of semiconducting SWCNTs. The third peak corresponds to the valence band conduction band transition of metallic SWCNT. Besides, Kim, D.Y. et al. [38], show that the optical absorbance increases with increasing average CNTs length. However, one of the power full analyses used to recognize both the existence and quality of SWCNTs is UV-visible and NIR spectra [43-45].

In the present work, UV-visible and NIR spectra for CNTs prepared at 700°C and 800°C were measured in the spectrum range 200 - 3000 nm. Figure 11 shows the UV-visible absorbance spectra for the prepared CNTs at temperatures 700°C and 800°C, respectively. Figure 12 shows the absorption spectra as a function of photon energy at NIR region. From Figure 12(a), one can clearly observe the characteristic peaks (peak I and peak II) for CNT at around 0.78 eV and 1.35 eV [44] when the preparation temperature is 800°C. Such results indicate that the prepared CNTs are mostly single walled type at least at preparation temperature of 800°C. Furthermore, the increase of the absorbance in Figure 12 when the
lengths are increased and as a result their aspect ratios are also increased [38]. From the above results, one can say that the optimum temperature for SWCNTs preparation with high aspect ratio is 800°C.

Chen D et al. [45] reported that semiconducting SWCNTs has a direct band-gap and the value of the optical energy gap is located in the range from 0.5 eV up to above 1.2 eV. In the present work we use Mott, Davis, and Tauc formula [46]:

\[
\alpha(\nu)h\nu = \begin{cases} 
\beta \left( h\nu - E_{opt} \right)^r, & h\nu > E_{opt} \\
0, & h\nu < E_{opt}
\end{cases}
\]

where \(\alpha(\nu)\) is the absorption coefficient, \(\nu\) is the frequency of light, \(\beta\) is a constant equals to \(\frac{4\pi\sigma_0/nc}{\Delta E}\), \(\sigma_0\) is the extrapolated DC conductivity, \(\Delta E\) is the energy gap tail (or energy which is interpreted as the width of the tail of localized states in the forbidden band gap), \(n\) is the refractive index, \(E_{opt}\) is the optical energy gap and \(r\) is an index. The value of \(r\) determines the type of electronic transition causing the optical absorption; it can take values 1/2, 3/2, 2, and 3 for direct-allowed, direct-forbidden, indirect-allowed, and indirect-forbidden transitions, respectively. It was found that the transition type is direct with \(r=0.5\) for both CNTs prepared at 700°C (Figure 13(a)) and 800°C (Figure 13(b)). The value of the optical energy gap is about 1.16 eV. This result is in a good agreement with those reported by Chen, D. et al. [45].

From the above analysis, we can say that the prepared CNTs are mainly semiconducting SWCNTs and the aspect ratio is clearly improved when the preparation temperature elevated up to 800°C.

3.5. Photoacoustic (PA) Measurements of Thermal Parameters

For thermal properties measurements of the samples at room temperature, the variation of the PA signal is observed at different chopping frequencies. This depth profiling was used for the measurement of the thermal diffusivity using the characteristic frequency \(f_c\) for each of the samples.

The main idea of PA technique is that the sample is placed in a closed chamber filled with a gas such as air and illuminated with monochromatic radiation of any desired wavelength, with intensity modulated at some suitable acoustic frequency; the non-radiative decay of the absorbed radiation results in a periodic heat diffusion from the sample to the air adjacent to the sample surface. This temperature variation produces a pressure fluctuation in the air within the cell which is detected as an acoustic signal by a sensitive microphone attached to the chamber. Accordingly, the PA signal contains informa-
Synthesis of Carbon Nano Tubes on Silicon Substrates Using Alcohol Catalytic Chemical Vapor Deposition

Figure 13. \((\alpha h)^2\) as a function of light energy for CNTs prepared at 700°C and 800°C.

It has been proved that the pressure variations depend on the relationship among three “length” parameters of the sample: the sample thickness \(\ell\), the optical absorption length \(\mu B\) and the thermal diffusion length \(\mu\). The pressure variations at the front surface of an optically opaque material \(\ell > \mu B\) can be written as the product of two terms, one depends on \(f\) and the other independent of \(f\). When \(f > f_c\) the variations of the frequency dependent term is independent of thermal diffusivity \(\alpha\) and when \(f < f_c\) the variations in PA signal depends on that can be calculated from [47]

\[
\alpha = \ell^2 f_c
\]

4. Conclusions

The preparation of catalyst using dip coating a silicon substrate into a diluted solution of cobalt acetate is studied as a function of time of dipping the substrate inside the solution and different heat treatment temperatures. The optimum time and temperature for preparing catalysts with nano particles with diameters ranging from 5 to 10 nm are 5 min and 400°C.

The growth of CNTs using the ACCVD method is performed as a function of growth temperature and at constant growth time, alcohol flow rate, catalyst concentration and carbon source. Carbon nanopowder is observed at preparation temperatures of 400°C and 500°C. Mixture of multiwalled carbon nanotubes and carbon nanopowder is achieved at a growth temperature of 700°C. Bundles of single walled carbon nanotubes with a little multwalled carbon nanotubes is achieved at a growth temperature of 700°C.
Figure 14. PA amplitude as a function of ln(f) for CNTs prepared at different temperatures.

ones are grown at 800°C. A majority of multiwalled nanotubes and little bundles of single walled CNTs are grown at temperature of 900°C. CNTs grown at temperature of 800°C are in the range of semiconducting
single walled carbon nanotubes with an optical energy gap of 1.16 eV and also, have maximum thermal conductivity of 170.4 (W/mK).

Besides, the features of the used technique lie in its easy, costless, and versatile nature in addition to its easiness to mount a small amount of catalytic metals by using diluted metal acetate solution. This method can be applied toward solids of various geometries without necessitating deposition/sputtering devices.

5. Acknowledgements

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REFERENCES


Table 2. Thermal diffusivity, effusivity and conductivity of prepared CNTs at different temperatures.

<table>
<thead>
<tr>
<th>Synthesis temperature (˚C)</th>
<th>Diffusivity (cm$^2$/s)</th>
<th>Effusivity (W/cm$^2$/°C)</th>
<th>Thermal conductivity (W/mK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>1</td>
<td>0.48</td>
<td>48</td>
</tr>
<tr>
<td>800</td>
<td>1.72</td>
<td>1.3</td>
<td>170.4</td>
</tr>
<tr>
<td>900</td>
<td>1.2</td>
<td>1.083</td>
<td>118.6</td>
</tr>
</tbody>
</table>

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