A Review on Low-temperature Carbon Nanotube Growth Methods to Improve Structural Control and Cost-efficiency

Sezin Su Elden, Barış Ulaş Önen,

Volkan Işık, Ahmet Hamdi Ünal

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INTRODUCTION

Carbon Nanotube (CNT) is a relatively new nanomaterial, which consists of graphene sheets rolled up together to form a cylindrical structure[1]. Due to their modifiable properties (optical[2], thermal[3], electrical[4], etc.), CNTs possess the possibility to be used in future technologies such as the enhancement of solar cells, battery electrodes, supercapacitors and flexible electronics[5] . However, CNT synthesis methods are still not satisfactory and being developed. There have been many methods developed, including arc discharge[6], laser ablation[7] , Chemical Vapor Deposition (CVD)[8] , given in the chronological order. We have focused our attention on CVD, a production method that involves heating feedstock gases to react chemically at a specific temperature[9]. CVD is a widely used method due to its suitability for industrial-scale synthesis and cost-efficiency[10]. There are especially two methods in CVD which have become prominent: Thermal CVD (TCVD) and Plasma Enhanced CVD (PECVD). These two methods are currently the most promising and researched ones, both having their advantages and disadvantages over one another; however, one of the main concerns related to them is their high temperature requirement[1], which is not efficient. Furthermore, a low-temperature growth is necessary for protecting the structural properties of CNTs as well as some specific applications like integrated circuit interconnects[11], stray light reduction[12] and optic lens production[2] . Thus, it is currently a major aim to reduce the synthesis temperatures further. In this paper, the most commonly used CVD methods TCVD and PECVD will be reviewed based on the purpose of operating at low temperatures. Further on, these methods will be evaluated comparatively by considering structural properties of CNTs, regarding the latest studies.

ANALYSIS OF CVD GROWTH METHODS

Thermal Chemical Vapor Deposition

Thermal Chemical Vapor Deposition (TCVD) is the chemical process of introducing different reactants into a reaction chamber, a vacuumed confined space, and decomposing a specific reactant onto a substrate at high temperatures. In CNTs synthesis, one of these reactants must be a carbonaceous compound (acts as carbon source) and the other must be a metallic one (acts as catalyst). There are no restrictions on the type of the substrate where the CNTs are formed in the end, but silicon, glass, and alumina are the most widely used ones[13]. Both reactants are transported by an inert gas, a type of gas that does not react with other materials, into the reaction chamber. After chemical reactions occur between carbonic and metallic reactants in the reaction chamber at high temperatures, chemically modified carbon *decomposes* onto the substrate in the form of a thin layer. This thin layer is where CNTs are *grown* (formed) at the end of this process[14].

Throughout the process, heat acts as the energy source of the overall system. Typical CNT synthesis with the TCVD method requires temperatures above 700°C[15] , and below this temperature is considered as low-temperature in the literature. Higher temperatures are mainly required to provide reaction energy for the reactants and improve the deposition rate, purity, density and crystallinity of the CNTs[14] . However, lower temperatures are more desired as we discussed in the introduction. Therefore, lowering temperature while improving CNT properties is one of the main concerns of the TCVD method in CNTs synthesis.

In the literature, the commonly appealed approach to lower temperatures in CNT growth by the TCVD method had been changing the catalysts. Unlike the previous studies, which mostly focus on the type of catalysts, a study[16] conducted by Shang et. al. also uses light during the growth process. This is an enhanced version of TCVD, which is known as Photo-Thermal CVD (PTCVD) in the literature. Shang et. al. studied how low the temperature could be dropped by using Ti/Fe as catalysts, C_2H_2 as the carbon source, Si as substrate and the light exposure technique. Their study revealed the lowest temperature possible as 370°C. Moreover, CNTs produced was 10 nm in diameter, 20 μm in length and had a growth rate of 1.3 μm/min. Although diameter and length values are in the typical range, growth rate value is greater (8-25 times) than conventional TCVD[16].

Shifting the focus to narrowing down the diameter of CNTs, another group of researchers[17] used Ni/SiO_2 as catalysts, CO as the carbon source, no substrate and no light exposure. Although they have focused on reducing the diameter, keeping the temperature as low as possible was still the main concern. This study achieved to reduce the diameter of CNTs to 0.8 nm at the expense of increasing the temperature to 500°C - which was still in the low-temperature range. He et. al.'s findings revealed that the larger diameter of CNTs are grown as the temperature applied gets higher in this setup. Besides, the use of CO as the carbon source is turned out to be effective in low-temperature CNTs synthesis.

In 2013, a group of researchers[18] remarked that the type of catalyst used and the concentration had a significant impact on the quality of the CNTs (He 2013). For the purpose of increasing the purity and controlling the structure under low temperatures, they experimented with different proportions of FeCu/MgO and CoCu/MgO. To evaluate the outcome, He et. al. used optical spectroscopic techniques for measuring chirality distribution and purity. The temperature they worked with was 600°C for the overall growth of CNTs as "low temperature" was not the sole purpose of the experiment. For instance, they have failed to grow CNTs at 600 °C on the monometallic Fe/MgO catalyst. Instead of changing the catalyst with a more expensive alternative or reducing the desired purity, they worked with higher temperatures relative to the previous studies. Consequently, the outcome indicated that unlike Fe nanoparticles, Co nanoparticles are more suitable for low-temperature growth of CNTs. In addition, the findings revealed that Cu nanoparticles play an important role in the facilitation of the reduction and inhibition of sintering the Fe nanoparticles in the desired low temperatures.

Developing the research over catalyst effect on low-temperature CNT synthesis, rather than using iron, a group of researchers[19] co-deposited cobalt nanoparticles and magnesium oxides . To take this research further, they addressed the problem of toxic or highly hazardous chemicals released during the process. This deposit was crucial for the simultaneous catalyzation of the decomposition of ethanol to spark the growth of CNTs. In order to address the problem of large diameters, which was the case in CNTs that grew below 400°C, this process reduced the diameter by 8 nm (from 20 nm to 12 nm) at 330°C. Basheer et. al. showed that the CNTs synthesized can be used for applications involving stray light reduction. Additionally, previous bidirectional measurements did not result in identical optical properties irrespective of underlying substrate - which is now possible.

Plasma-enhanced Chemical Vapor Deposition

Plasma-enhanced CVD is a chemical deposition process that works at lower temperatures (below 500 °C) relative to other CVD methods[21]. The difference between PECVD and other CVD methods is that the reactant gas is excited to plasma, which is a carbon source in the case of

CNT growth[20]. A typical PECVD includes two parallel plate electrodes laying inside a vacuum chamber. A potential difference between these electrodes is created by either a DC or AC source[21]. The gas molecules get excited when introduced between these electrodes. The excited gas becomes a substance consisting of free electrons, ions and radicals. The final substance is called a plasma. The carbon source is very energetic after turning into the plasma state. The high energy carbon source readjusts itself to a CNT structure by the end of various chemical reactions with the help of a catalyst. The reactions can occur at lower temperatures because the carbon source is already very energetic[21]. Although PECVD requires lower temperatures to grow CNTs, there are some limitations over this method. This technique can reduce the control over the growth of CNTs. Besides, PECVD can cause structural defects[20]. Moreover, a high temperature can still be required to convert the carbon source to plasma and to activate the catalyst. Although this temperature is lower than other CVD methods, it is important to further lower the temperature to obtain higher quality CNTs more efficiently. Thus, lowering the temperature of the PECVD process while protecting and controlling the CNT structure remains a challenge today.

The study[22], conducted by Wang et. al., published in 2010 two methods for plasma enhanced CVD (PECVD) are compared: radio frequency and direct current PECVD. These methods are used to grow CNTs on glass substrates. These two methods (RF-PECVD and DC-PECVD) are different two powering options to produce plasma. The significant difference comes from their nature. DC-PECVD creates an electric field that accelerates the electrons very fast through the positive planes. In RF-PECVD the average electric force on the electrons is zero. So, RF-PECVD has higher electron density which means higher ionization rate. As a result, under the condition of 30W, 10 SCCM CH4 and 180°C, height of 1.6 μm CNTs with diameter range of 10-30 nm are produced by RF-PECVD. Under the same conditions CNTs didn't grow on DC-PECVD. They grew in the conditions of 50W, 15SCCM CH4 and 180°C by dc-PECVD but they were only 0.2 μm in length. Also in the study, Wang et al. compared FeNi and Fe as catalysts and they showed that FeNi is more suitable for CNT growth. So, the result is that CNTs can be grown more efficiently by RF-PECVD with FeNi thin film catalyst than DC-PECVD.

Another study[23] ,conducted by Tabatabaei et. al., published in 2011, introduced a new method for PECVD growth of CNTs. In this method, the system has a two-stage plasma consisting of alternative current (AC) and direct current (DC) powered plasmas. This method is used to grow CNTs on glass substrates like in the first study[22]. In the system, AC plasma is used to heat the atoms to create ions, electrons and radicals. Radicals are crucial because of their longer lifetime than ions or electrons. In the second stage DC plasma is used to grow CNTs directly on the glass substrate. As a result, under the conditions of 35 SCCM acetylene and below 400°C, CNTs grew. These CNTs have a length of 2 μm and diameters less than 100 nm. In the study, Ni catalyst deposited on In-Sn Oxide/glass substrate. So, the study introduced a new way to grow CNTs under the conditions below 400 °C and it is possible to grow CNTs, which are longer than it is in the first study.

A research group led by Xiaochao et. al. developed a novel way of growing CNTs by implementing an active screen plasma (ASP) technique to a preexisting RF-PECVD system[24]. An active screen plasma is a technique that is used to treat alloys. In this study, ASP was used for developing the catalyst layer over the substrate without an additional step. The absence of the additional step lowered the production cost and improved the efficiency of the overall CNT growth. There are two additional benefits of including ASP. ASP provided a protective layer that protected the growing CNT from the plasma damage. The protective layer allowed the CNTs to grow at lower temperatures. Also, ASP contributed to the heating process by increasing the thermal radiation inside the chamber. Unlike the previous studies [22,23], this one[24] used a multi-metal alloy - consisting of Fe, Co and Ni - as a catalyst. With the addition of ASP and a multi-metal catalyst, CNTs were grown at low growth temperatures between 400 and 500 °C. The diameter of the resulting CNTs were inversely proportional to the growth temperatures. The average diameter of the CNTs formed at 400, 450 and 500°C were 28 nm,23 nm and 16 nm respectively. So, study 7 showed that implementing an ASP into a PECVD and using a multi metal catalyst results in a cost-effective and efficient low temperature PECVD method.

In addition to lowering the growth temperature, a study by Debojyati et. al. also focused on controlling CNT's diameters[25]. The diameter of the CNTs can also be controlled by adjusting the size of the nanoparticles that forms the catalyst. In particular, the diameter of the CNTs can be decreased by using a smaller catalyst. The study used a low-temperature wet chemical method to produce Fe catalyst in a desired form. The CNTs were grown with a microwave PECVD with 600W of microwave power. A predesigned shadow mask was used for accelerating the plasma, hence increasing the CNT growth. With the addition of the shadow mask and the control over the catalyst allowed a diameter controlled growth of carbon nanotubes at low temperatures around 300°C. The diameter of the CNTs ranged from 10 to 100 nm. The outcome suggests that the RF-PECVD method can be used as a low-temperature growth method for CNTs while controlling the diameter.

CONCLUSIONS

In this paper, we have presented two most common CNT production methods: TCVD and PECVD. In essence, they differ on the energy source they use. TCVD uses thermal energy to start a chemical reaction while PECVD uses internal energy of the plasma. The main focus while reviewing these methods was lowering the temperature while having control over the geometric structure, orientation, and individual nanotube manipulation, purity to lower the expenses and increase the performance. To achieve this, the following parameters are adjusted in general:

- Catalyst (type and production method)
- Light exposure
- Plasma type
- Active Screen Plasma (ASP) addition

The relationship between catalyst and growth-temperature is still not clear, and the future studies must be conducted to identify it. Also, we do not have total control over the structure such as the diameter of the CNTs. How they are influenced by the temperature change should also be investigated in further research. Currently, although it is not the only concern as we discussed, PECVD has managed to reach lower reaction temperatures[22] when compared to TCVD[16,17,18,19]. Today, scientists have more control on CNTs' structural properties in low-temperature with lower costs. However, efficiencies of both the heating process of TCVD and the plasma production of PECVD must be increased in order to lower the temperature further. The future of the research is based on improving these methods even further. Therefore, as we did not encounter any alternative approach, it is highly probable that these two methods will be dominating the near future of the field.

Cited References

1. Ahmad M, Silva SRP. Low temperature growth of carbon nanotubes – A review. Carbon. 2020 [accessed 2020 July 17];158:24-44. https://doi.org/10.1016/j.carbon.2019.11.061.
2. He X, Htoon H, Doorn SK, Pernice WHP, Pyatkov F, Krupke R, Jeantet A, Chassagneux Y, Voisin C. Carbon nanotubes as emerging quantum-light sources. Nature Materials. 2018 [accessed 2020 July 19];17:663-670. https://doi.org/10.1038/s41563-018-0109-2.
3. Ji T, Feng Y, Qin M, Feng, W. Thermal conducting properties of aligned carbon nanotubes and their polymer composites. Composites Part A: Applied Science and Manufacturing. 2016 [accessed 2020 July 19];91(1):351-369. https://doi.org/10.1016/j.compositesa.2016.10.009.
4. Gong S, Zhu ZH, Meguid SA. Anisotropic electrical conductivity of polymer composites with aligned carbon nanotubes. Polymer. 2015 [accessed 2020 July 19];56:498-506. https://doi.org/10.1016/j.polymer.2014.11.038.
5. Abdalla S, Al-Marzouki F, Al-Ghamdi AA, Abdel-Daiem A. Different Technical Applications of Carbon Nanotubes. Nanoscale Research Letters. 2015 [accessed 2020 July 19];10(358). https://doi.org/10.1186/s11671-015-1056-3.
6. Maria KH, Mieno T. Synthesis of single-walled carbon nanotubes by low-frequency bipolar pulsed arc discharge method. Vacuum. 2015 [accessed 2020 July 19];113:11-18. https://doi.org/10.1016/j.vacuum.2014.11.025.
7. Chrzanowska J, Hoffman J, Melolepszy A. Synthesis of carbon nanotubes by the laser ablation method: Effect of laser wavelength. Physica Status Solidi B. 2015 [accessed 2020 July 19];252(8):1860-1867. https://doi.org/10.1002/pssb.201451614.

8. Sharma R, Sharma AK, Sharma V. Synthesis of carbon nanotubes by arc-discharge and chemical vapor deposition method with analysis of its morphology, dispersion and functionalization characteristics. Cogent Engineering. 2015 [accessed 2020 July 19];2(1):1094017. https://doi.org/10.1080/23311916.2015.1094017.

9. Pirard S, Douven S, Pirard JP. Large-scale industrial manufacturing of carbon nanotubes in a continuous inclined mobile-bed rotating reactor via the catalytic chemical vapor deposition process. Frontiers of Chemical Science and Engineering. 2017 [accessed 2020 July 19];11:280-288. https://doi.org/10.1007/s11705-017-1635-1.

10. Yanase T, Miura T, Shiratori T, Weng M, Nagahama T, Shimada T. Synthesis of Carbon Nanotubes by Plasma-Enhanced Chemical Vapor Deposition Using Fe1−xMnxO Nanoparticles as Catalysts: How Does the Catalytic Activity of Graphitization Affect the Yields and Morphology?. C. 2019 [accessed 2020 July 19];5(3):46. https://doi.org/10.3390/c5030046.

11. Nessim GD. Encyclopedia of Nanotechnology. Heidelberg (GERMANY): Springer Netherlands; 2012. [accessed 2020 July 19]. https://doi.org/10.1007/978-90-481-9751-4_244.

12. Hagopian JG, Getty SA, Quijada M, Tveekrem J, Shiri R, Roman P, Butler J, Georgiev G, Livas J, Hunt C, Maldonado A, Talapatra S, Zhang X, Papadakis SJ, Monica AH, Deglau D. Carbon Nanotubes, Graphene, and Associated Devices III. Bellingham (WA): SPIE; 2010. [accessed 2020 July 19]. https://doi.org/10.1117/12.864386.

13. Handuja S, Srivastava P, Vankar VD. On the Growth and Microstructure of Carbon Nanotubes Grown by Thermal Chemical Vapor Deposition. Nanoscale Research Letters. 2010 [accessed 2020 July 19];5(1211). https://doi.org/10.1007/s11671-010-9628-8.

14. Dahmen KH. Encyclopedia of Physical Science and Technology. 3rd edition ed. San Diego (California): Academic Press; 2003 [accessed 2020 July 17]; 787-808. https://doi.org/10.1016/B0-12-227410-5/00102-2.

15. Malekimoghadam R, Rafiee R. Carbon Nanotube-Reinforced Polymers. Elsevier; 2018 [accessed 2020 July 17];41-59. https://doi.org/10.1016/B978-0-323-48221-9.00003-0.

16. Shang NG, Tan YY, Stolojan V, Papakonstantinou P, Silva SRP. High-rate low-temperature growth of vertically aligned carbon nanotubes. Nanotechnology. 2010 [accessed 2020 July 17];21(50):505604. https://doi:10.1088/0957-4484/21/50/505604.

17. He M, Chernov AI, Obraztsova ED, Sainio J, Rikkinen E, Jiang H, Zhu Z, Kaskela A, Nasibulin AG, Kauppinen EI, Niemelä M, Krause O. Low Temperature Growth of SWNTs on a Nickel Catalyst by Thermal Chemical Vapor Deposition. Nano Research. 2011 [accessed 2020 July 17];4:334-342. https://doi.org/10.1007/s12274-010-0088-3.

18. He M, Chernov AI, Obraztsova ED, Jiang H, Kauppinen EI, Lehtonen J. Synergistic effects in FeCu bimetallic catalyst for low temperature growth of single-walled carbon nanotubes. Carbon. 2013 [accessed 2020 July 19]; 52:590-594. https://doi.org/10.1016/j.carbon.2012.10.029

19. Basheer HJ, Pachot C, Lafont U, Devaux X, Bahlawane N. Low‐temperature thermal cvd of superblack carbon nanotube coatings. Advanced Materials Interfaces. 2017 [accessed 2020 July 19];4(18):1700238. https://doi.org/10.1002/admi.201700238

20. Hamedani Y, Macha P, Bunning TJ, Naik RR, Vasudev MC. Plasma-enhanced chemical vapor deposition: where we are and the outlook for the future. 2016 [accessed 2020 July 19]. https://doi.org/10.5772/64654

21. Meyyappan M. A review of plasma enhanced chemical vapour deposition of carbon nanotubes. J. Phys. D: Appl. Phys. 2009 [accessed 2020 July 19]; 42(21):213001. https://doi.org/10.1088/0022-3727/42/21/213001

22. Wang H, Moore JJ. Different growth mechanisms of vertical carbon nanotubes by rf- or dc-plasma enhanced chemical vapor deposition at low temperature. J. Vac. Sci. Technol.. 2010 [accessed 2020 July 19]; B 28:1081-1085. https://doi.org/10.1116/1.3497030.

23. Tabatabaei MK, Ghafouri fard H, Koohsorkhi J, Khatami S, Mohajerzadeh S. Remote and direct plasma regions for low-temperature growth of carbon nanotubes on glass substrates for display applications. Journal Of Physics D: Applied Physics. 2011 [accessed 2020 July 19]; 44(115401):1-8. http://dx.doi.org/10.1088/0022-3727/44/11/115401.

24. Xiaochao Ji XJ, Wei Zhang WZ, Xiaoying Li XL. A novel hybrid method combining ASP with PECVD for in-situ low temperature synthesis of vertically aligned carbon nanotube films. Diamond & Related Materials. 2017 [accessed 2020 July 19]; 77:16-24. http://dx.doi.org/10.1016/j.diamond.2017.05.008.

25. Debajyoti Das DD, Ajay Roy AJ. Synthesis of diameter controlled multiwall carbon nanotubes by microwave plasma-CVD on low-temperature and chemically processed Fe

nanoparticle catalysts. Applied Surface Science. 2020 [accessed 2020 July 19]; 515:146043. https://doi.org/10.1016/j.apsusc.2020.146043