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Effect of the Carbon Source Flow Rate on the Quality of the Growth of Super-Aligned Carbon Nanotube Arrays by the Chemical Vapor Deposition Method

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ABSTRACT

In this study, carbon nanotubes were fully aligned by chemical vapor deposition at atmospheric pressure on a silicon substrate at two carbon source flow rates of 28 and 38 sccm (standard cubic centimeter per minute). Acetylene gas (C_2H_2) as the carbon source for argon gas (Ar) as the carrier gas for hydrogen gas (H_2) for the recovery of the nanoparticle and iron nanoparticles as the catalytic source at 800 °C were used for the growth of the carbon nanotube array. The reaction was carried out in a 48 cm long quartz tube and the gases were injected with specified flow rates. The silicon substrate was coated by the magnetic sputtering method with catalytic iron nanoparticles with a thickness in the range of 3-6 nm. The results of the FESEM analysis showed, as the carbon source flow rate was increased to 38 sccm, the average diameter of the grown carbon nanotubes is increased, and the carbon nanotubes with a diameter of 60-70 nm were most abundant.

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1. Introduction

Carbon nanotubes have a one-dimensional structure because of the larger length than their diameter. Carbon nanotubes have both molecular and solid properties. Of the carbon nanotube structures discovered, the two structures have received the most attention. These two structures include single-walled carbon nanotubes discovered in 1991 and multi-walled carbon nanotubes discovered in 1993 [1]. The length of the carbon nanotubes is about 100 to several 100s microns, and the carbon nanotubes are about 1 to 50 nanometers in diameter. Single-walled nanotubes are

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graphite plates that are cylindrically wrapped. The diameter of the cylinder is between 1 and 50 nm. The outer diameter of the multiwalled nanotubes is about 2 to 25 nm, and their inner diameter is about 1 to 8 nm. The average length of multi-walled nanotubes such as graphite mass between the graphite-separated layers, in which there is no three-dimensional order, can also be several micrometers [2]. They are steam. The first two methods are less important due to the difficulty of controlling the process and the discontinuity of the process as well as the cost of the required tools compared to chemical vapor deposition. Also in these methods the growth of nanotubes in a certain direction is not possible [3]. Chemical vapor deposition at atmospheric pressure in addition to the ability to control the growth of nanotubes is a simple and economical way to produce carbon nanotubes at low temperatures and ambient pressure [4 and 5]. In the chemical vapor deposition method, a type of hydrocarbon gas, such as methane, acetylene, etc. (as a carbon source), is broken by heat in the presence of a catalyst and the resulting carbon sits on a substrate as carbon nanotubes [6]. The selection of metal catalysts may affect the growth and morphology of the nanotubes [4, 7]. A large number of metals have been used as catalysts for the growth of high temperature carbon nanotubes [8]. But the most used metals to succeed in the growth of nickel-cobalt carbon nanotubes and bimetallic iron-molybdenum catalysts are due to not only the high solubility of carbon in these metals compared to other high temperature intermediate metals but also the carbon emission rates in these metals. More carbon nanotubes arrays are perfectly aligned with nanotubes that are synthesized in a uniform fashion. The array growth of a fully aligned array allows the nanotubes to have unique electrical and mechanical properties. A key characteristic of array-based carbon nanotubes is that the continuous laminates are composed of a thin layer comprising parallel pure carbon nanotubes [9–14]. The requirement for these vertically aligned nanotubes to be applied to horizontal thin films is that the nanotubes have perfectly smooth and van der Waals interaction surfaces [10]. These laminates, which by their very nature are distinct from randomly grown carbon nanotubes and are parallel to each other by forming thin films, are produced as strong conductors with the high light transmittance. Many potential applications of these nanotubes have been demonstrated, for example as polarizers; transparent conductive films and polarized light sources [9 and 12]. However, in the future these sheets may be compressed into dense fibers, which may have high tensile strength and high Young's modulus [14 and 11]. Plus they are good choices for electron emission sources [7]. There is no doubt that more applications of these types of sheets will be discovered in the future. However, there are two major challenges to finding widespread applications of carbon nanotube sheets. The first challenge in how to scale up the synthesis of carbon nanotubes is that they include expanding array levels and achieving batch growth. In 2005, a team of researchers succeeded in synthesizing perfectly aligned carbon nanotubes on a silicon film with the diameter of 4in in the low pressure chemical vapor deposition (LPCVD) [10]. Despite these findings, the fact that only synthesized coherent array carbon nanotubes, including multi-walled carbon nanotubes with diameters in the range 10 to 15 nm, are able to form coherent sheets remains the same [9–14].

In this study, carbon nanotubes are fully aligned by chemical vapor deposition at atmospheric pressure on a silicon substrate at two carbon source flow rates of 28 and 38 sccm.

2. Materials and methods

2.1. Materials

2.1.1. Silicon substrate (Si)

Silicon (Si) substrates with the p-type (100) characteristic are used to layer the catalytic structure, having 1 × 1 cm dimensions and 500 μm thickness (Fig. (1)).

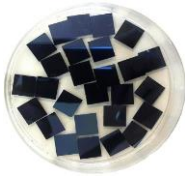


Figure 1. Schematic of silicon substrate (Si) with p-type (100) characteristic.

2.1.2. Chemical vapor deposition apparatus

The device used in this study for the growth of an array of carbon nanotubes is a completely one-way chemical vapor deposition device with atmospheric pressure that has two hot zones (two growth sites) with the length of 24 cm (Fig. (2)). In addition, the device comprises a quartz tube with a length of 48cm , internal diameter of 4.2cm and external diameter of 4.8cm . In this study, the hot zone near the inlet of the gases is used to further influence.

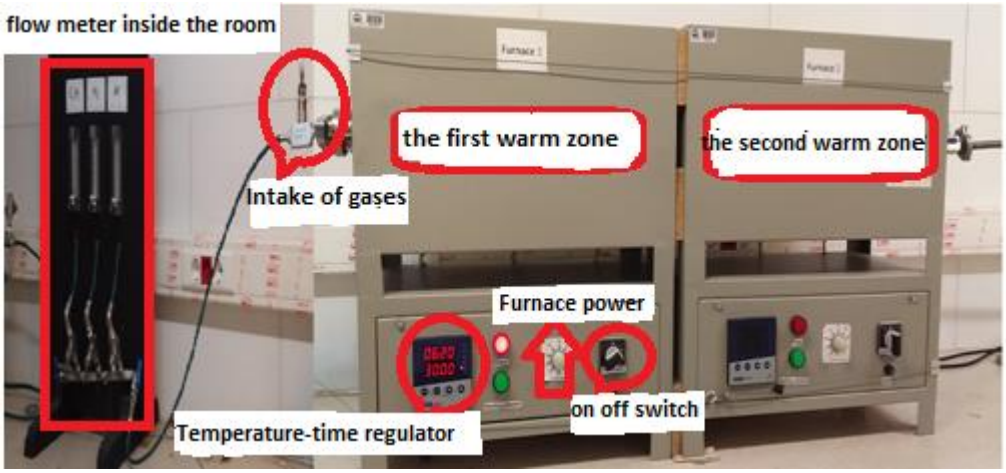


Figure 2. Chemical Vapor Deposition (CVD) device.

2.2. Methods

2.2.1. Layering method

For the substrates to be coated with iron nanoparticles, the substrates need to be completely clean. For this purpose, silicone substrates first cut into 1 × 1 cm pieces were placed in an acetone-containing vessel (to clean the surface) for 15 minutes in an ultrasonic bath and then washed with deionized water and then repeated with isopropanol. Finally, nitrogen gas was used to dry the substrates. After cleaning the substrates, their substrates were bombarded with iron target by magnetic sputtering.

The use of sputtering for the manufacture of a thin film was first reported in 1852 and then it has been economically and scientifically insignificant [15]. In the sputtering process, the target surface is bombarded with high-energy particles (50–1000 eV) (Fig. 3) [15]. As a result of the impact of high-energy particles on the target, the target atoms are excited.

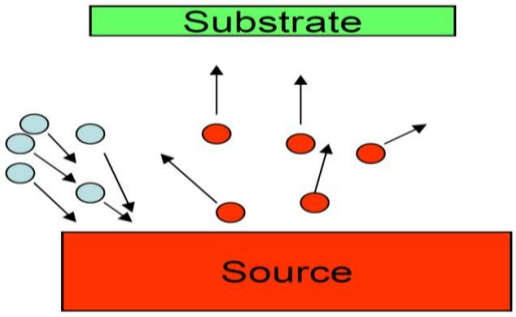


Figure 3. Target Surface Bombardment in the Spattering Process [15].

Different types of sputtering include diode sputtering, magnetron sputtering, magnetic sputtering, and ionic beam spattering. The most common and precise layered method is magnetic sputtering. Since the growth of carbon nanotubes as a whole array requires a high-precision and fully dense layering, this method was used in this study. The magnetic field used in this method increases by increasing plasma density, the current density at the target or cathode, resulting in an increase in the sputtering rate. Fig. 4 shows the substrate layered with 3-6 nm thick iron nanoparticles by magnetic sputtering.

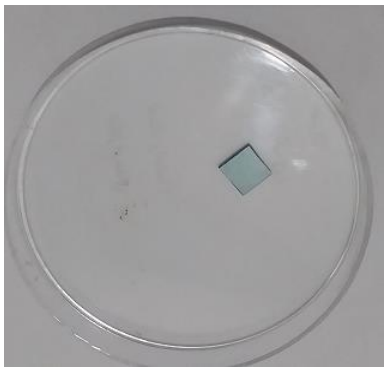


Figure 4. View of the layered substrate by magnetic sputtering.

2.2.2. General Method of the Test

The purpose of this study was to determine the optimum amount of carbon source flow rate to improve the quality of super-aligned carbon nanotube arrays grown on the silicon substrate deposited by iron nanoparticles. For this purpose, the main reaction chamber, which is a quartz tube, is placed inside the furnace at a specified temperature (depending on the type of experiments) and the reaction gases are introduced into it. The carbon source used in this study is acetylene gas (C_2H_2). Argon (Ar) gas is also used as the carrier gas and hydrogen gas (H_2) is used to recover nanoparticles. These gases are injected into the quartz tube using flowmeters located at their specified flow rates (depending on the type of experiments).

To investigate the effect of carbon source flow rate on the quality of the growth of super-aligned carbon nanotube arrays. First, the gas cylinders containing the carbon source, hydrogen gases and argon are opened. The purpose is to regulate the flow of gases as well as ensuring that the gas is contained within the cylinders (as shown in Fig. 2). Then all valves inside the chamber are tighten and then the screws on both sides of the furnace are tighten after inserting the substrate with iron nanoparticles (by magnetic sputtering) in the middle of the furnace (the middle of the hot area near the gas inlet or the furnace flame location). Then, before the furnace power is switched on, the time-temperature steps of the furnace must be defined. Then step 1 is adjusted for 50 min and 800 °C and step 2 for 35 min (5 min for hydrogen gas fluxing and the rest time for growth by acetylene carbon source). Finally, the third step is seted to reduce the temperature to 50 °C at 20 min. In the first step, argon gas enters the quartz tube until the furnace temperature reaches 800 °C over a period of 50 min. In the second step, simultaneously with the argon gas flowing in 352 sccm and hydrogen gas flowing in 26 sccm, the substrate (iron nanoparticles reduction) was regenerated. The flows with the rates of 28 and 38 sccm for the growth of super-aligned carbon nanotube arrays flow separately on three layered silicon substrates. The carbon source current will then be cut off and, in the final step (step 3), in the presence of the flow of argon gas, the furnace temperature will be reduced to 50 °C at 20 min.

2.2.3. Results analysis method

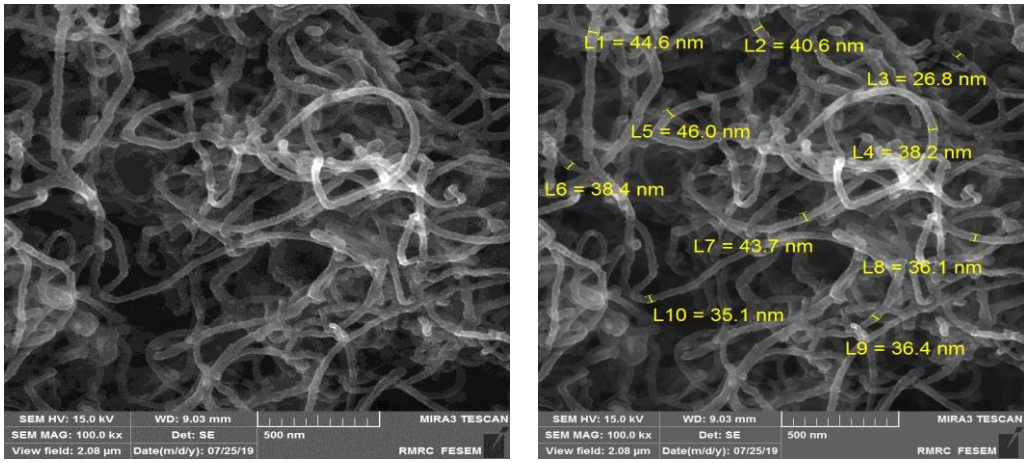
In this study, the field emission scanning electron microscopy (MIRA3TESCAN-XMU) model is used to analyze the results of the growth of carbon nanotubes more precisely [16]. In the conventional electron microscopy,

tungsten filament is used as a source of the electron beam production, which has little power to concentrate the electron beam on the target and therefore reduces the image resolution. With a very high focus on the target area and high magnification of about 750000 times the image quality is still maintained. The new generation of field emission electron microscopes, due to the high centralization power of the emitted electron column, can also examine samples that contain oxides or other contaminants.

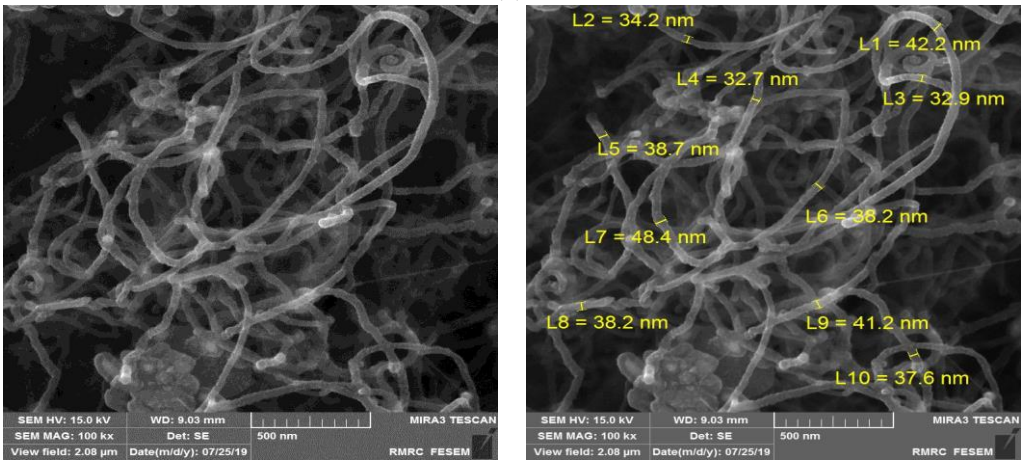
3. Results and discussion

3.1. Investigation of the effect of the flow rate of the carbon source on the growth of super-aligned carbon nanotube arrays

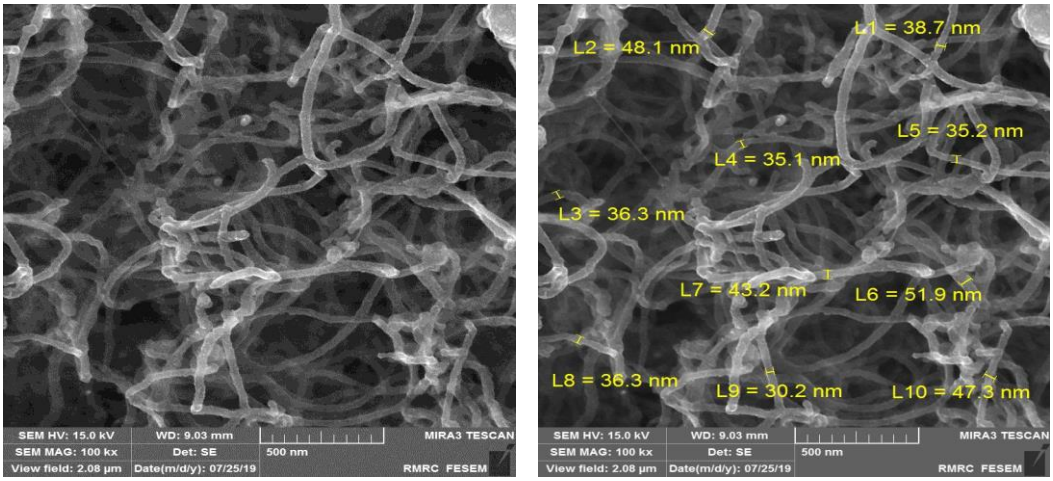
Fig. 5 shows the FESEM images of the various surface spots of an array of carbon nanotubes grown on a silicon substrate coated with iron catalytic nanoparticles at a flow rate of that of acetylene carbon source equal to 28 sccm. In addition, in each of the images the outer diameter of some of the nanotubes is specified. As it can be seen in this figure, the diameter distribution of carbon nanotubes grown at a high level is in the range of 26.8-46 nm (Fig. 5 (a)), 32.7-48.4 nm (Fig. 5 (b)) and 30.2-51.9 nm (Fig. 5 (c)), which can be reduced at lower levels of the mean diameter of the nanotubes. However, at high levels, carbon nanotubes with diameters in the range of 10-25 nm are also found (Fig. 6). It can also be seen from Fig. 6 that carbon nanotubes with diameters in the range of 35-40 nm have the highest percentage.



(a)



(b)



(c)

Figure 5. FESEM images of the different surface spots of carbon nanotube arrays grown on a silicon substrate coated with iron catalytic nanoparticles at a flow rate of 28 sccm of the carbon source.

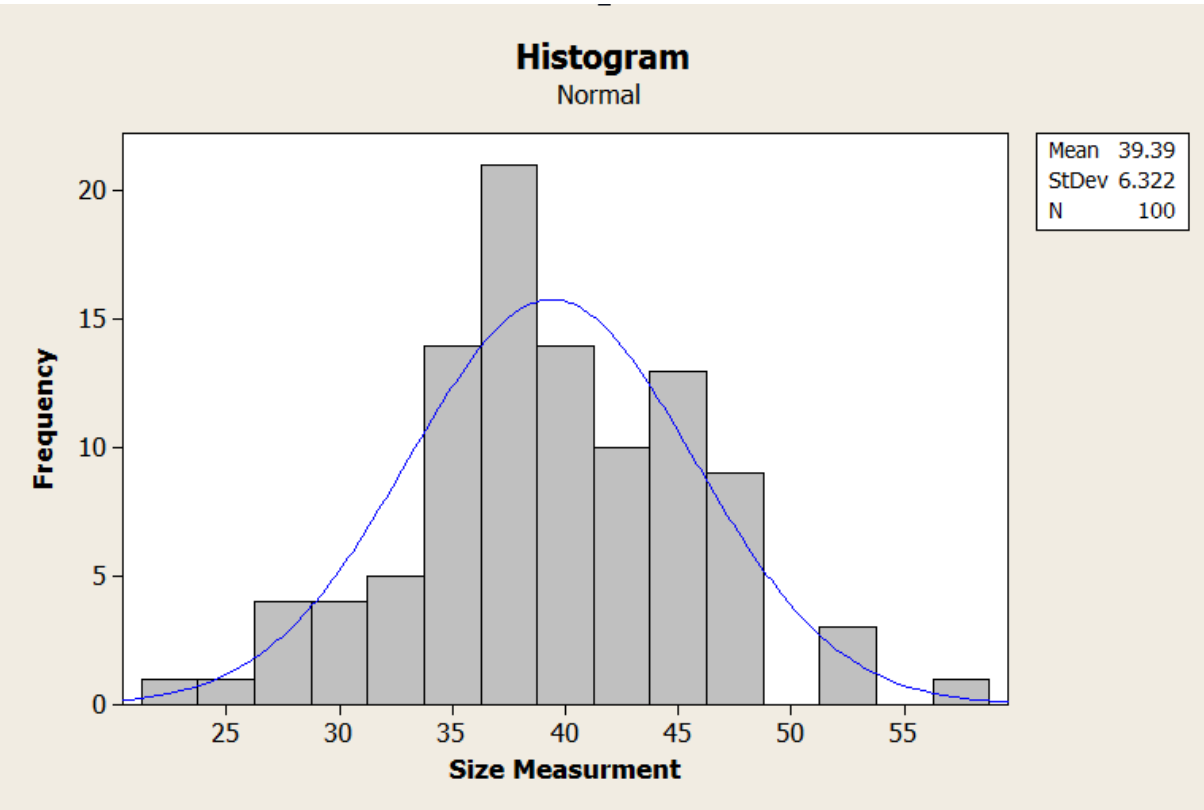
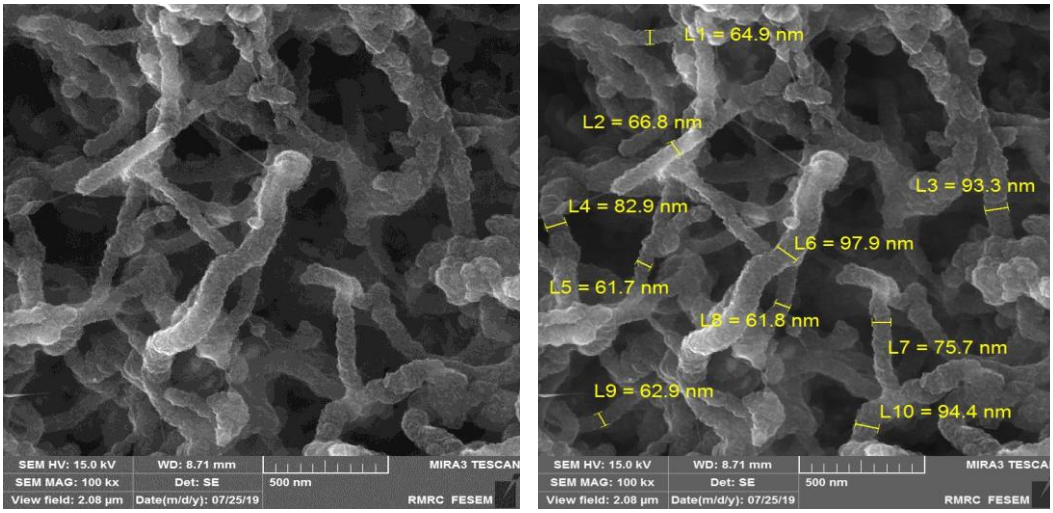
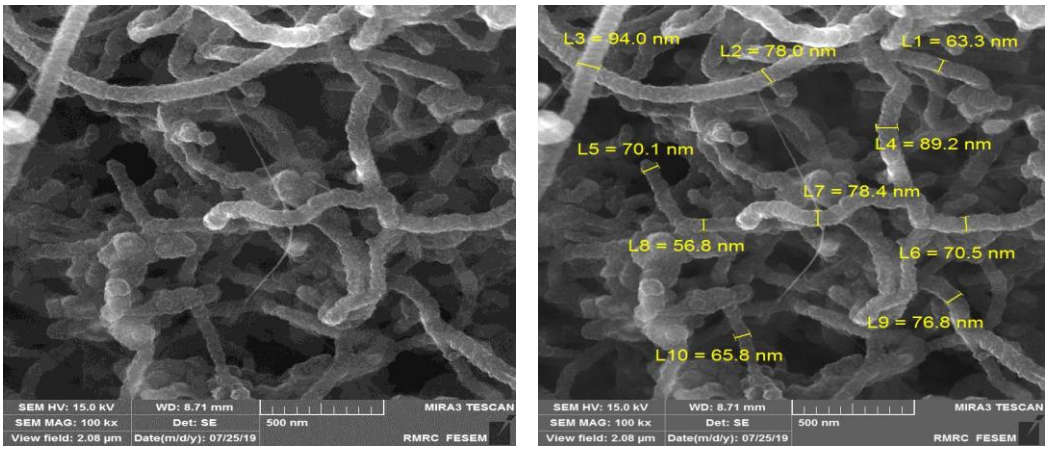


Figure 6. Frequency distribution diagram of carbon nanotube arrays grown on a silicon substrate at a flow rate of 28 sccm of the carbon source.

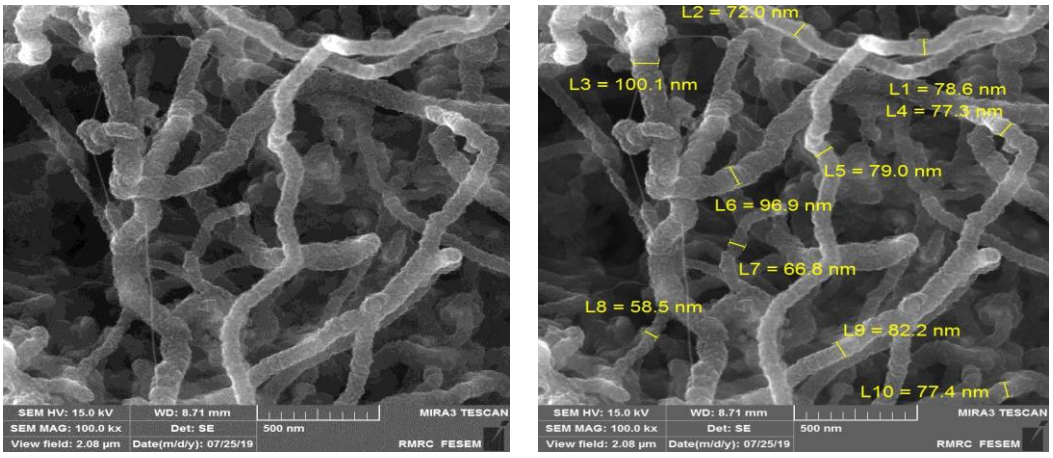
However, as the flow rate of the carbon source increases to 38 sccm, the average diameter of the grown carbon nanotubes increases (Fig. 7), in which case carbon nanotubes with the diameters of 60-70 nm are most abundant (Fig. 8). Since carbon nanotubes with diameters in the range 10-15 nm are capable of forming perfectly aligned array sheets, therefore, increasing the carbon source flow rate decreases the possibility of perfectly aligned array sheets.



(a)



(b)



(c)

Figure 7. FESEM images of different surface spots of carbon nanotube arrays grown on a silicon substrate coated with iron catalytic nanoparticles at a flow rate of 38 sccm of the carbon source.

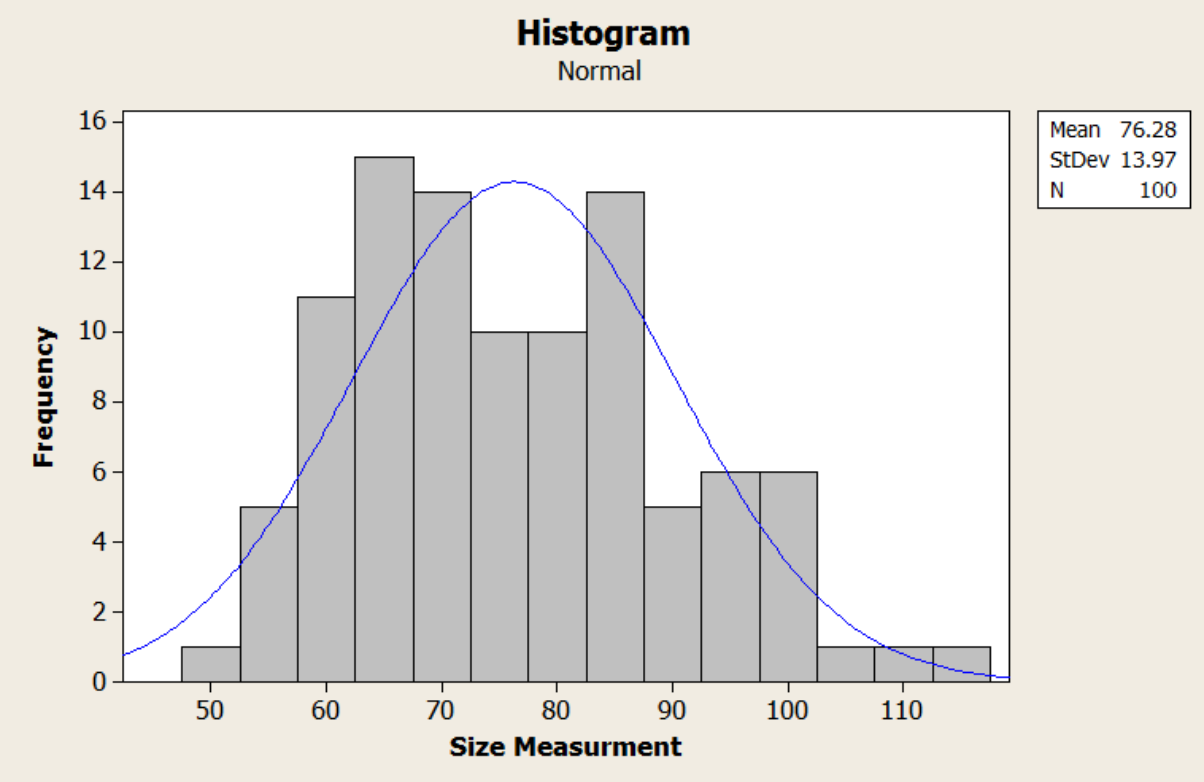


Figure 8. Frequency distribution diagram of carbon nanotube arrays grown on a silicon substrate at a flow rate of 38 sccm of the carbon source.

4. Conclusion

Carbon nanotubes were grown completely in one direction with atmospheric pressure chemical vapor deposition in the flow rates of 28 and 38 sccm of the carbon source. In this method, silicon substrate layered with iron nanoparticles was used by the magnetic sputtering method. The results of the FESEM analysis showed that by increasing the flow rate of the carbon source, the average diameter of the grown carbon nanotubes increased significantly, which reduced the possibility of forming regular array sheets. In addition, as the flow rate of the carbon source improved, the density of the grown-up carbon nanotubes decreased.

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