CHAPTER 2

Theoretical Background

2.1 Introduction

The carbon nanotubes are currently the focus of intensive research due to their unique properties and potential to impact broad research of science and technology *(C. L. Cheung and et al., 2002).* Materials with modified nanostructures surface have attracted great attention in the last decade because of their numerous applications such as medicine micro channel plate's technology (MCP) *(N. A. Grigoryeva. et al, 2007),* filtration, and hydrogen sensors *(S. Shingubara., 2003).* The most common parameter derived from surface studies of the fractal analysis is the fractal dimension D_d that is a direct geometric implication in relation to other material parameters found in various applications *(S.V. Muniandy. et al, 2003).* There are six basic methods of measuring fractal properties the box counting method, adsorption studies, chord-length measurements, and correlation function measurements, small angle scattering and spectral methods *(D. R. Vollet Donatti, et al,2006).*Such that; the fractal dimension is a measure the roughness of a surface *(J. Hayashi, et al. 2002).* Previous study was used the change of palladium/Anodic Aluminum Oxide Pd/AAO membrane structure using fractal approach *(H.Idriss, et al, 2009)* For an image with embedded fractal objects (namely the Pd aggregates), the number of covering boxes scales as N (l) ~ l–D, where D is fractal dimension *(T. Nychyporuk., et al., 2005).* Here, a direct visualization of these microstructures can be done using the concept of surface roughness *(H. Idriss., et al., 2009).*All these topics will be discussed in this chapter.

2.2   Catalyst Used For CNT Growth

A catalyst is described as a substance that increases the rate at which a chemical reaction approaches equilibrium without itself becoming permanently involved in the reaction *(Richardson 1989).* But the main role of catalyst in CNT growth is to decompose hydrocarbon molecules *(Dupuis 2005).* The catalyst material is one of the most important key parameters, and determines the morphology, type (SWNT or MWNT), diameter and also growth mechanism in the production of CNTs. CNT formation is affected by method of catalyst preparation *(Bonadian, et al. 2006),* the nature and pore size of the support *(Qingwen, et al. 2002),* and the nature of the metal *(Ago, et al. 2006),* the quantity of active catalyst particles and size distribution of the active component *(Atike İnce, 2010)* assist on CNTs formation.

Major of studies in the literature is about CNT growth. Several hydrocarbon gases were examined for CNT growth by CVD method. However, acetylene was reported to produce mostly multi walled carbon nanotubes MWNT material among them. Many catalysts are investigated for CVD and the results show that mixture of transition metals are more efficient than monometallic catalyst for CNT growth. Especially, Fe and Co catalysts are reported for high quality CNT formation. Metal-supported catalysts are appropriate for CNT growth. As support, inorganic porous materials such as silica (SiO_2), alumina ($Al2O_3$), zeolites and magnesium oxide (MgO) are generally used *(Chai, et al. 2006).* In a previous study; common catalyst preparation methods used for CNT growth are impregnation, sol-gel and combustion. Among these methods, impregnation method generally gives SWNT and DWNT. The most promising support material is MgO for this method because of great number of alkaline reaction sites that it possesses. It gives high yield of SWNT and DWNT almost without any defect when it supported Fe-Mo bimetallic catalyst *(Yoshihara, et al. 2007).* Sol-gel method produces catalysts with high surface area, high porosity and ultra-low density. The interaction between catalyst particles and support materials is very strong at this method; therefore it is also appropriate for SWNT growth. Different from impregnation method, Al_2O_3 is the most efficient support for sol-gel method due to the strong acidity on the surface of Al_2O_3

material. CNTs grown over catalyst produced by combustion method are generally MWNTs and they are thicker than CNTs grown over catalysts prepared by impregnation and sol-gel methods. As a conclusion, Co-Mo/MgO catalyst prepared by gel-combustion method was chosen for previous study, this method is a modified sol-gel method *(Rashidi, et al. 2007)*. The advantage of this method is to give catalyst which has a high yield of surface area and give a good dispersion that is why obtained CNTs are at high quality and high yield. In order to increase specific surface area, different organic compounds such as tartaric acid, citric acid, ethylene diamine tetraacetic acid (EDTA), and sorbitol can be used. Among these organic additives, sorbitol derived catalyst gives the highest specific surface area and the smallest metal particle size *(Rashidi, et al. 2007)*, current study used Fe and Co Nanopowder catalysts for CNT production and characterizations. Fe or Co CNTs produced and annealed at different temperatures 450ºC, 650ºC, 850ºC, and 950ºC and gases flow rates 10,20,30,40 sccm C_2H_2, 50 sccm H_2, 100 sccm Ar respectively. It was observed that catalyst material consists of quite large particles. Particles sizes were in the range of 40- 250μm. And the iron and cobalt nanotubes diameter was found at the range of 2~3nm. Therefore, the Fe or Co catalyst particle size proportional to the CNTs growth and heating variations at LPCVD system and gases of H_2, C_2H_2, Ar different flow rates.

2.3   Carbon Nanotubes

By rolling a graphene sheet into a cylinder and capping both end of the cylinder with a half of fullurene molecule a carbon nanotube is formed. Harry Kroto discovered C60 molecule in 1985 *(Kroto, et al. 1985)*. Type of carbon nanotube is determined by the number of the concentric graphene layers.

2.3.1   Type of Carbon Nanotubes

Carbon nanotubes are categorized as single wall carbon nanotubes and multi wall carbon nanotubes. If carbon nanotube contains one graphene layer, it is named single wall nanotube (SWNT); whereas if it contains two or more concentric layer, it is called multi wall carbon nanotube (MWNT).

2.3.1.1 Single- Wall Carbon Nanotube (SWNT)

A single-wall carbon nanotube (SWNT) is defined by a graphene sheet rolled into a cylindrical shape with a diameter of about 0.4-10 nm and lengths extending up to several microns. If we ignore two ends of carbon nanotube and focus on the large aspect ratio of the tube, carbon nanotubes can be considered as one-dimensional nanostructures with axial symmetry and they have excellent properties because of this symmetry *(Baddour, et al. 2005)*. Depicted in figure 2.1.

2.3.2.2 Multi -Wall Carbon Nanotube (MWNT)

The second type consists of tubes made of more than one concentric graphene cylinders coaxially arranged around a central hollow with a constant interlayer spacing, which is nearly equal to 0.34 nm *(Dresselhaus, et al. 2001),* graphite layer spacing, and called multi-shell or multi-wall carbon nanotubes (MWNT) and MWNTs consist of 2 to 30 concentric graphene, diameters of which range from 2.5 to 100 nm. MWNTs are stronger than SWNTs, but they have more defects than SWNTs *(Dai, 2002).* Depicted in figure2.3.1.
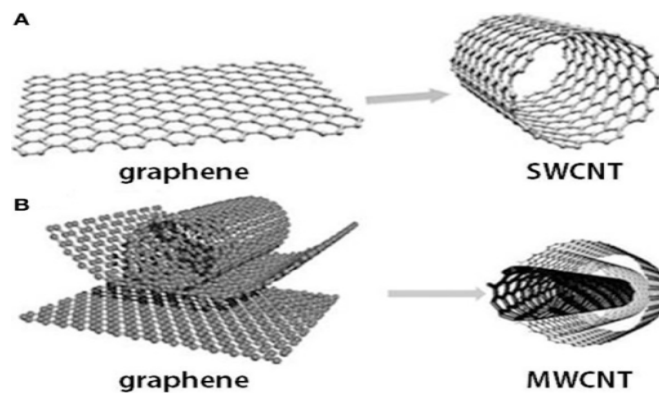

Figure 2.3.1 SWNTs, and MWNTS Schematic Diagram (Source: Dai, 2002)

2.4 Morphology of Carbon Nanotubes

There are several methods to synthesize CNT, the most common techniques are discharge *(Journet, et al. 1997),* laser ablation *(Thess, et al.1996),* and chemical vapor deposition (CVD) *(Niu, et al. 2006)* methods.

2.4.1 Arc discharge method

The first carbon nanotubes are produced with arc discharge method *(Iijima 1991).* This method has been used for synthesis of single-wall carbon nanotubes, multiwall nanotubes, and ropes of single-wall nanotubes *(Journet, et al. 1997).* This method is the process of CNT growth on carbon (graphite) electrodes by applying direct current (DC) in an inert gas such as argon or helium *(Popov 2004).* Figure 2.4.1 is a schematic illustration of the arc-discharge setuper with large concentration of amorphous carbon and CNTs are not aligned.
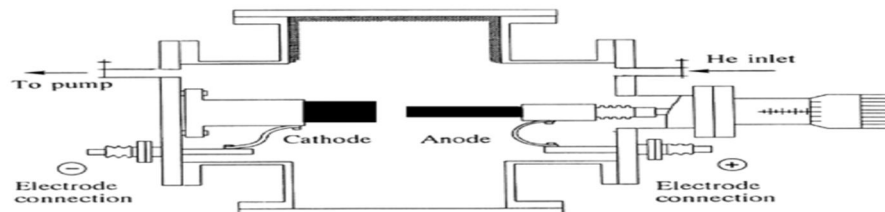

Figure 2.4.1 Cross sectional view of a arc generator (Source: Harris 2007)

In this method, there are two high-purity graphite electrodes of 5-20 mm diameter separated by 1 mm. A voltage of 20-25 V is applied across the electrodes and a dc electric current of 50-120 A flows between the electrodes. When applying current, temperature reaches to about 4000ºC, anode vaporises and condenses on the cathode surface, so the length of anode decreases with increasing the formation of carbon

nanotubes . During the process both electrodes are cooled with water and the arc is generally operated in He atmosphere at low pressure between 50-700 mbar. By the arc discharge method carbon nanotubes synthesis can be done with or without catalyst in order to produce multi-wall carbon nanotubes and single-wall carbon nanotubes, respectively *(Journet and Bernier 1998).*

For multi-wall carbon nanotube production, there is no catalyst need, and nanotubes are found in bundles in the inner region of the cathode deposit and are roughly aligned in the direction of electric field *(Ebbesen, et al. 1993, Seraphin, et al. 1993).* Using this method Iijima produced first multi-wall carbon nanotube in 1991, and these nanotubes had 2 to 50 walls. However, many products also occur at this method such as fullerenes, amorphous carbon and graphite sheets *(Baddour 2005).* By heating the growth material in oxygen environment, graphitic particles can be oxidized and purification is provided, but oxidation also removes an substantial amount of nanotubes. When one of the graphite electrodes (anode) contains a transition metal catalyst particles such as Fe, Co, Ni, single wall carbon nanotubes can be synthesized using arc discharge method. First single-wall carbon nanotube synthesis by arc discharge method was reported in 1993 by *Iijima and Ichihashi,* and the used catalyst was Fe in their study. In the same year Bethune et al. also synthesized single- wall carbon nanotubes with this method, but using Co as a catalyst. There are a lot of study about single-wall carbon nanotube synthesis but the results always change, it can be said that experimental conditions and catalyst species effects the results. As a conclusion, arc discharge is the most common and simplest method to produce carbon nanotubes, but it require a purification, and which the purification is the main disadventage of this method, during this process carbon nanotubes might be damaged.

2.4.2 Laser ablation method

It is the second method and it can provide arrays of ordered CNTs. The first carbon nanotube synthesis by laser ablation method was reported by Guo *(Guo, et al. 1995).* This method utilizes an intense laser pulse *(Yudasaka, et al. 1999)* or a continuous laser *(Maser, et al. 1998)* to ablate a Co-Ni/graphite composite target. The target is placed in a

tube furnace heated to 1200ºC. When this target vaporizes, a cloud of C, C_2, C_3 and catalyst vapors occur, then cloud condenses, and the small amount of carbon species come together to form a larger one. The vaporized catalysts prevent the closing of these carbon molecules into cage structure, so the growth process is finished with the formation of a single-wall carbon nanotube *(Scott, et al. 2001, Baddour and Briens 2005)*. During the laser ablation, an inert gas (generally helium or argon) flow take place in the growth chamber and provides grown carbon nanotubes to collect on a water-cooled cupper collector as shown in figure 2.4.2. Laser has a very high energy density so this method is appropriate to evaporate materials that have high evaporation temperature *(Ando et al. 1994)*. With increasing laser power, target temperature increases, hence the yield of carbon nanotubes improves.
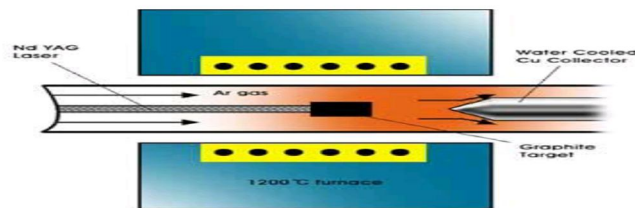

Figure 2.4.2.Schematic illustration of a laser ablation apparatus *(Source: Daenen, et al. 2003)*

Relatively high purity single-wall carbon nanotube synthesis is the main advantage of laser ablation method. With this technique, multi-wall carbon nanotube synthesis has not been reported yet. On the other hand, scale-up is not possible with this method because of very high temperature and capital cost need.

2.4.3 Chemical Vapor Deposition CVD Method

The last technique is CVD technique which is appropriate for scaling-up. While arc discharge and laser ablation methods require a solid target and very high temperatures to evaporate it, CVD method can be used at lower temperature, and the CNTs obtained from both with arc discharge and laser ablation methods are tangled ; thus purification is not evident for these methods. The general nanotube growth mechanism in a chemical vapor deposition process through the dissociation of hydrocarbon molecules over the transition metal nanoparticles, dissolution and saturation of carbon atoms in these nanoparticles. CVD method has been used first for the production of carbon filaments more than 4 decades ago *(Walker, et al. 1959),* however, it was utilized to grow multi-wall carbon nanotubes till 1993 *(Yacaman, et al. 1993).* Some different CVD techniques have been developed for carbon nanotube growth such as plasma enhanced CVD, thermal CVD, alcahol catalytic CVD, laser assisted CVD and aero-gel supported CVD. Thermal CVD method will be explained later in details. Carbon nanotube growth includes two main steps; the first one is the catalyst preparation and the other one is the nanotube growth on this catalyst. In order to synthesis nanocatalyst particles, a thin film layer can be used by annealing or a catalyst can be synthesized by some chemical methods. At the first step, prepared catalyst sample is placed in a quartz tube which is in a furnace and the temperature is set to a desired point. During the increase of the temperature to the set point, an inert gas flow takes place through the tube to prevent the oxidation of samples. When the furnace reaches to the desired temperature a preannealing can be done with H_2 to reduce catalyst nano particles from oxide form to metal form. The other step is sending hydrocarbon gas to the system as a carbon precursor. Generally used hydrocarbon gases are CH_4, C_2H_4, C_2H_2, C_6H_6 for carbon nanotube growth *(Cui, et al. 2003).* During growth process, hydrocarbon gas decomposes and carbon deposits onto the catalyst. Carbon has a low solubility in these metals at high temperature and therefore the carbon precipitates to form cabon nanotubes. The key parameters in nanotube growth by CVD are the catalyst system, temperature, composition and the flow rate of the carrier and hydrocarbon gases *(Biris, et al. 2006).* The particle structure and composition also are very important parameters to explain the differences observed between the nanotubes morphologies

(Loiseau, et al. 2003). In CVD method Fe, Co, Ni transition metals or their alloys are used as catalyst to synthesize carbon nanotubes. As support, inorganic porous materials such as silica (SiO_2), alumina (Al_2O_3), zeolites and magnesium oxide (MgO) are generally used *(Liu, et al. 2004)*. CVD is the most preferred method to produce carbon nanotubes, because this method is performed at low temperature compared with the other methods *(Reich et al. 2004)*. The other reason is this method allows controlling the diameter of CNTs by controlling catalyst nanoparticles size *(Weifeng, et al. 2003)*. At the same time it is easy to perform CVD process. Another reason is that it is suitable method for large scale production *(Yacaman, et al. 1993, Weifeng, et al. 2003)*. The schematic illustration of CVD system is depicted in Figure 2.4.3.
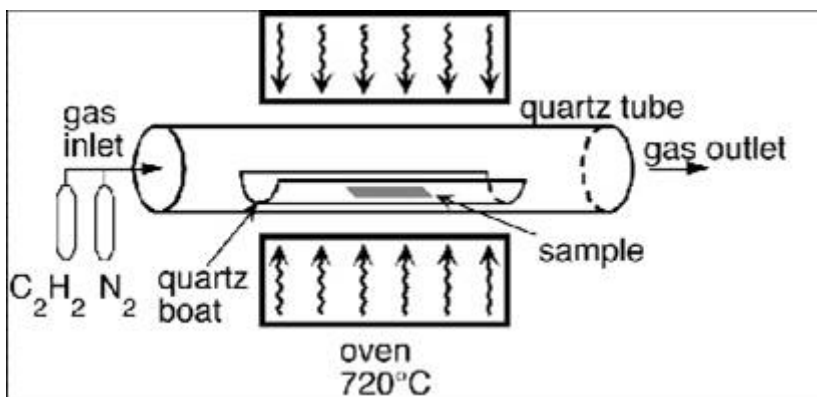

Figure 2.4.3 The schematic illustration of CVD system *(Source: Daenen, et al. 2003)*

There are two types of CNT growth mechanism. The first one is the base growth in which the metal catalyst particle stay at the end of the tube. The other growth type is the tip growth in which the metal catalyst particle might remove from the surface and moves at the top of the growing carbon nanotube *(Dupuis 2005)*. The interaction between catalyst particle and support is stronger at base growth mechanism than tip growth mechanism so catalyst particle remains attached to the support *(Dupuis 2005)*.

LPCVD method was used to synthesize CNT. Shown in figure 2.4.3, the system consists of two parts, first part is a Lindberg/Blue M 1100 ºC Split Mini Furnace and the other part is its controller. All experiments were done at a high temperature so samples in a quartz boat were placed in a 1 inch diameter quartz tube. The upper temperature limit of the furnace is 1100 ºC. Quartz boat used to carry catalyst particles into oven. CNT growth

14

experiments researchs were performed at atmospheric pressure. Firstly, a catalyst pretreatment took place with Ar, H_2 or Ar-H_2 mixture keeping the total gas flow at 100 sccm for 20 min at 100 to 850 ºC. Ar gas sent into the system to remove the contamination and to prevent the oxidation of the samples, and H_2 gas sent into the system to prevent amorphous carbon formation and to provide the reduction from metal oxide catalyst to metal catalyst which are more suitable for CNT growth. After reaching to the desired temperature C_2H_2 gas flow was started to initiate the CNT growth. Ar and H_2 continued to flow during CNT growth. The total gas flow was 100, 50 sccm respectively at CNT growth. Different gas flow rates for Ar, H_2 and CH_4 were investigated. In this study growth temperature in the range of 450 to 950ºC was studied. Growth time was also another parameter for the CNT growth, growth times were investigated, at 20 min. When the growth was finished, first the hydrocarbon gas was turned off but H_2 gas and Ar gas was still flowing through the system and the temperature was set to 0 ºC so the system was left for cooling under again Ar, H_2 or Ar-H_2 mixture ambient.

2.5 Carbon nanotubes Application

Carbon nanotubes have attracted the fancy of many scientists worldwide. The small dimensions, strength and the remarkable physical properties of these structures make them a very unique material with a whole range of promising applications *(Pulickel M. Ajayan,et al. 2016).* In this review we describe some of the important materials science applications of carbon nanotubes. Nanotubes can be used in the electronic and electrochemical applications, nanotubes as mechanical reinforcements in high performance composites, nanotube-based field emitters, and their use as nanoprobes in metrology and biological and chemical investigations, and as templates for the creation of other nanostructures. Also; carbon nanotubes are being considered for energy production and storage. Graphite, carbonaceous materials and carbon fiber electrodes have been used for decades in fuel cells, battery and several other electrochemical applications (R. L. McCreery,1991)
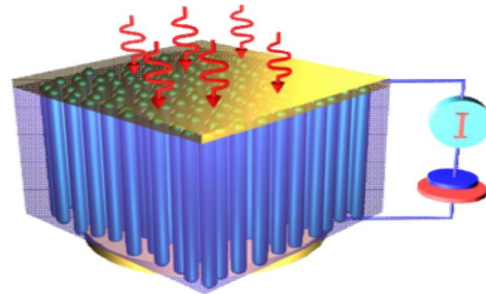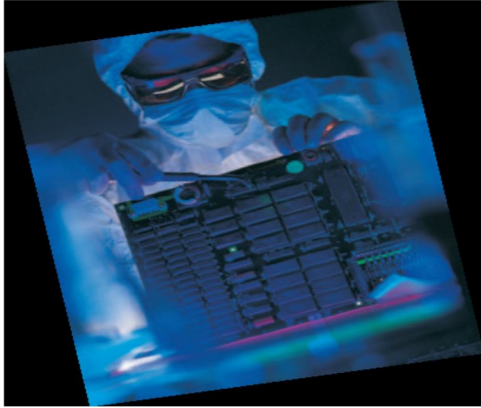
Fig.1 Schematic drawing of the photoconductivity measurement in Ge nanowire array inside AAO.

Figure 2.5 Carbon nanotubes application in Electronic & Semiconductor Device material *(Source: H. Idriss, 2009)*

Challenges and potential for Carbon Nanotube Applications have come a long way since their discovery in 1991. The structures that were first reported in 1991 were MWNTs with a range of diameters and lengths. These were essentially the distant relatives of the highly defective carbon nanofibers grown via catalytic chemical vapor deposition. The real molecular nanotubes arrived when they were found accidentally while a catalyst (Fe, Co) material was inserted in the anode during electric-arc discharge synthesis. For the first time, there was hope that molecular fibers based purely on carbon could be synthesized and the excitement was tremendous, since many physical properties of such a fiber had already been predicted by theory. It was really the theoretical work proposed on SWNTs and the availability of nanoscale technology (in characterization and measurements) that made the field takes off in 1991. As a novel material, fullerenes failed to make much of an impact in applications. It seems, from the progress made in recent research, that the story of nanotubes is going to be very different. There are already real products based on nanotubes on the market, for example, the nanotube attached AFM tips used in metrology. The United States, Europe and Japan have all invested heavily in developing nanotube applications. Nanotube-based electronics tops this list and it is comforting that the concepts of devices (such as room-temperature field-effect transistors based on individual nanotubes) have already been successfully demonstrated. As in the case of most products, especially in high technology areas, such as nano-electronics, the time lag between concept demonstration and real products could be several years to decades and one will have to wait and see how long it is going to take nanotube electronics to pervade high technology. Other more

obvious and direct applications are some of the bulk uses, such as nanotube-based polymer composites and electrochemical devices. These, although very viable applications, face challenges, as detailed in this review. What is also interesting is that new and novel applications are emerging, as for example, nanotubes affecting the transport of carriers and hence luminescence in polymer-based organic light-emitting diodes, and nanotubes used as actuators in artificial muscles. It can very well be said that some of these newly found uses will have a positive impact on the early stages of nanotube product development.

As a conclusion; this review has described several possible applications of carbon nanotubes, with emphasis on materials science-based applications. Hints are made to the electronic applications of nanotubes which are discussed elsewhere. The overwhelming message we would like to convey through this chapter is that the unique structure, topology and dimensions of carbon nanotubes have created a superb all-carbon material, which can be considered as the most perfect material that has ever been fabricated. The remarkable physical properties of nanotubes create a host of application possibilities, some derived as an extension of traditional carbon example fiber applications, but many are new possibilities, based on the novel electronic and mechanical behavior of nanotubes. It needs to be said that the excitement in this field arises due to the versatility of this material and the possibility to predict properties based on its well-defined perfect crystal lattice. Nanotubes truly bridge the gap between the molecular realm and the macro-world, and are destined to be a star in future technology.

2.6 Fractal Analysis Method

The term fractal from the Latin adjective fractus. The corresponding Latin verb frangere means "to bretlk:" to create irregular fragments. It is therefore sensible- and how appropriate for our needs for that, in addition to "fragmented" (as in fraction or refraction), fractus should also mean "irregular," both meanings being preserved in fragment. The proper pronunciation is fractal. The stress being placed in fraction. The combination fractal set will be defined rigorously, but the combination natural fractal will serve loosely to designate a natural pattern that is usefully representable by a fractal set. For example, Brownian curves are fractal sets, and physical Brownian motion is a natural fractal. (Since

algebra derives from the Arabic jabara = to bind together, fractal and algebra are etymological opposites!). The fact that the basic fractals are dimensionally discordant can serve to transform the concept of fractal from an intuitive to a mathematical one. We choose to focus on two definitions, each of which assigns to every set IRE in Euclidean space, no matter how "pathological," a real number which on intuitive and formal grounds strongly deserves to be called its dimension. A fractal is by definition a set for which the Hausdorff Besicovitch dimension strictly exceeds the topological dimension. Every set with a non integer D is a fractal. Incidentally, Felix Hausdorffs name being given to a class of topological spaces, the widely used contracted term for 0, Hausdorff dimension, seems to have undertones of "dimension of a Hausdorff space," thus suggesting it is a topological concept- which emphatically is not the case. This is yet another reason for preferring fractal dimension.

In the last several years, fractal properties of porous media have attracted considerable attention, and many theoretical, computer simulation, and experimental studies have been under taken in attempt to understand it. There are six basic methods of measuring fractal properties the box counting method, adsorption studies, chord-length measurements, and correlation function measurements, small angle scattering and spectral methods *(Sahimi, M. 1995)*. Such that; the fractal dimension is a measure of roughness of a surface *(Hayashi, J. et al, 2002)* were used several methods of measuring. For example; fractal dimension used as a guide to setting the threshold for converting dark field images this can used to support the existence of a preferred orientation in a thin film (Ag), or to get quantitative information about the phase content of multi-phase films *(Dannenberg, 2002)*. In previous study were used mass fractal characteristics of the material (wet gel and aerogel) to determine the 'pore' volume distribution evaluated from N_2 adsorption obtained from SAXS data *(Vollet et al., 2006)*.

However, material image analysis employs a wide variety of techniques to perform morphological as well as textural analysis in order to rapidly count, measure, and/or classify features such as particles, fibers, or structural elements appearing in an image. The primary use of SEM is the study of the surface topography of solid samples that would be enhanced with the adaptation of fractal techniques in microstructure image

interpretation.

2.6.1 Box counting method or Grid covering method

- ✓ The SEM photograph was converted to image in form of box counting images (or Digital Image). In a 2D structure comprised of pixels.
- ✓ a "matrix" composed of *n* rows and *m* columns where each pixel location is denoted by the index *(i, j)* For: $0 \leq I < n$ and $0 \leq j < m$

0,0	0,1	…	0,m
1,0	1,1	…	1,m
. . .	. . .	. . .	. . .
n,0	n,1	…	n,m

Figure2.6.1 Box counting method or Grid covering method

(Source: Daenen, et al. 2003)

Box dimension:

- ❖ The Fe, Co CNTs microstructure images bellowed were analyzed using program HarFA 5.1.
- ❖ The SEM images have been converted to binary image (Binarization) were covered with different grids (box length ε), and the number of boxes N(ε) required to cover the structures of the images is recorded
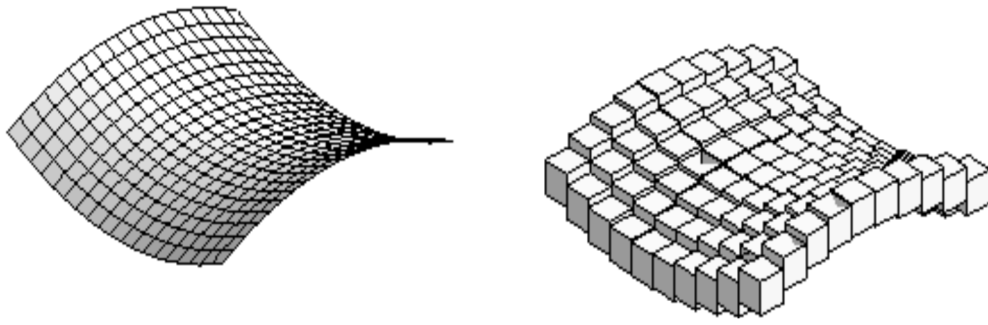
19

Figure 2.6.2 Box dimension *(Source: Daenen, et al. 2003)*