UNIVERSITI TEKNIKAL MALAYSIA MELAKA

INFLUENCE OF SOLUTION PROCESS PARAMETER TO IRON CATALYST THIN FILM AND PARTICLE FORMATION

This report submitted in accordance with requirement of the Universiti Teknikal Malaysia Melaka (UTeM) for the Bachelor Degree of Manufacturing Engineering (Engineering Material) (Hons.)

by

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2014

APPENDICES

ABSTRACT

Solution process or sol-gel process is the most reliable process to produce thin film compared to the other process such as chemical vapor deposition and physical vapor deposition. The process is easy and can be done in ambient temperature without the needs of any vacuum chamber and on top of that, it is cost effective. The process can be divided into two stages which are spin coating and heat treatment. The results from spin coating and heat treatment processes are expected to be the uniform thickness of thin film and the particle formation, respectively. Therefore the needs of finding suitable parameter for the spin coating process is very demanding due the suitable parameter will lead to uniform thickness of thin films. Spin speed is one of the parameter that influences the uniformity of the thin film. Heat treatment is the next process to promote the formation of catalyst particles. The heat treatment temperature is also influences the size of the particles form on the substrate. The results from this experiment are a uniform thin film and also the particle size that form is below ten nanometers.

ABSTRAK

Proses larutan atau proses "*sol-gel*" adalah proses yang paling boleh diharapkan dalam penghasilan lapisan filem nipis berbanding proses lain seperti pemendapan wap kimia dan pemendapan wap fizikal. Proses ini boleh dijalankan dalam keadaan normal tanpa perlu keadaan kedap dan ia juga adalah proses yang murah untuk dijalankan. Proses ini terbahagi kepada dua bahagian iaitu putaran lapisan dan rawatan haba. Keputusan daripada proses putaran lapisan dan rawatan haba adalah lapisan filem nipis yang sekata dan pembetukan zarah (*particle*). Oleh itu, parameter yang sesuai adalah amat perlu yang akan memberi keputusan kepada filem nipis yang sekata. Kelajuan pusingan proses spin coating adalah salah satu parameter yang memberi kesan kepada penghasilan filem nipis yang sekata. rawatan haba pula adalah proses yang menggalakan pembetukan zarah pada catalyst filem nipis. Saiz pembentukan zarah pula adalah dipengaruhi oleh proses rawatan haba. Hasil daripada eksperimen ini ada pembentikan lapisan filam yang nipis dan pembentukan zarah yang bersaiz bawah sepuluh nanometer.

DEDICATION

To my beloved family, I have devoted all my effort in order to accomplish this PSM 1 report. The reason why I devote all my effort in this report is because I want my family to know especially my beloved mother madam Azizah that I have done my best in order for me to full fill all bachelor degree program. On top of that, I dedicate this report to my supervisor which has helping me throughout this whole semester to complete my full thesis.

ACKNOWLEDGEMENT

Syukur Alhamdulillah, our god Allah to still allow the breath flowing in my body and let me completes this PSM 1 report. I would like to thank my supervisor Dr Mohd Asyadi Azam that help me a lot and guide me to complete the first part of the whole program of PSM. Not forgotten, the Master student, Miss Najiha and my entire class mate who help me in giving idea on how to tackle some issue regarding this report. On top of that, to my family that has fully supported me since I start my journey as a degree student in UTeM

CHAPTER 1

INTRODUCTION

1.1 Background

In today's world, the dependent on development of high tech electronic devices is very high and the use of carbon nanotubes (CNTs) is one of the best solutions for miniaturizing electronic beyond by basis of modern technology. Although the CNT is promising to enhance the electronic device performance, but due to the high cost of CNTs, the application of CNTs in electronic devices is still limited. In a way to lead to the growth of CNTs, the catalyst thin film needs to be produced and the formation of particle is vital. The fabrication of thin film using solution process which use spin coating and heat treatment is really ensuring due to the process is done without any vacuum process, low cost, large deposition, simple equipment and the most importantly is, it can be done in normal atmosphere compare to other process such as electron beam deposition and physical vapor deposition.

1.1.1 Carbon nanotube (CNT)

The main motivation of this project is the needs to form particle from thin film that will next be used to grow CNTs. CNTs is a material with a shape of tube, which made of carbon that has a diameter in nano scale size (Kumar and Ando, 2010). The capacity of CNT is having an high thermal conductivity with outstanding current carrying capacity and have high flexibility of CNTs promise to resolve problem in the connect area, with the low operative electron and hole mass. The attractiveness band gap and the lack of dangling bonds indicate the needs of a fast, energy efficient and high dielectric suitable device for the future (Kreupl, 2008). Other than that, CNT have a unique nanostructure with remarkable mechanical properties (Medhekar, 2004). The following interest was the promise that the remarkable structure and properties of carbon nanotubes might give rise to some unique applications.

CNT shows a combination of strength, stiffness and firmness as compared to other fiber materials which usually lack one or more of these properties. Thermal and electrical conductivity are also very high, and comparable to other conductive materials.

Table 1.1: Mechanical Properties of Engineering Fiber. (nanocyl 2013)

Fiber Material	**Specific Density**	**E (TPa)**	**Strength (GPa)**	**Strain at Break (%)**
Carbon Nanotube	1.3 - 2	1	10 - 60	10
HS Steel	7.8	0.2	4.1	< 10
Carbon Fiber – PAN	1.7 - 2	0.2 - 0.6	1.7 - 5	0.3 - 2.4
Carbon Fiber – Pitch	2 - 2.2	0.4 - 0.96	2.2 - 3.3	0.27 - 0.6
E/S - glass	2.5	0.07 / 0.08	2.4 / 4.5	4.8
Kevlar* 49	1.4	0.13	3.6 - 4.1	2.8

Table 1.2: Transport Properties of Conductive Materials. (nanocyl 2013)

Material	**Thermal Conductivity (W/m.k)**	**Electrical Conductivity**
Carbon Nanotubes	> 3000	106 - 107
Copper	400	6 x 107
Carbon Fiber - Pitch	1000	2 - 8.5 x 106
Carbon Fiber - PAN	8 - 105	6.5 - 14 x 106

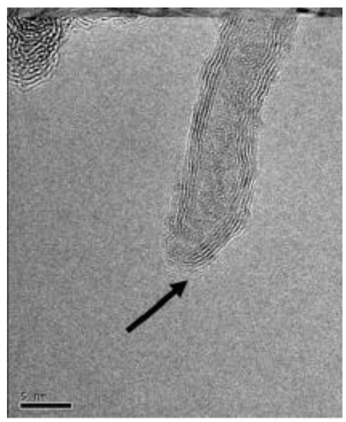

Figure 1.1: CNT growth by CCVD with scale 5nm. (Wang et al, 2007)

There are many ways to growth CNTs and the most applied technique is CVD. As compared to arc-discharge and laser-ablation methods, CVD is a simple and economic technique for synthesizing CNTs at low temperature as compared to other techniques. (Kumar and Ando 2010). But before the CNTs can be growth using CVD system, the thin film need to be form on the substrate first to form catalyst nanoparticles. The usual method to form a thin film on the substrate is PVD but the main problem for PVD is the cost to form a thin film is high. The use of spin coating process is really promising due to its large deposition and it is less expensive.

1.2 Problem statement

The formation of catalyst thin film for CNT usually accomplish by using physical vapor deposition (PVD) due to the proses able to produce a uniform thin film. Even though the process have high capability in producing such uniform thin film, most of manufacturer still looking for other methods to replace an existing proses. This is prior to energy consumed by the process. The PVD process also need to done in a vacuum system. Due to this entire factor, it increased the total operating cost which leads to an expensive cost of product

Spin coating process is the best ways in order to resolve this problem. Even though the proses is promising, the process are still lacking in the control of the uniformity of the thin film and the particle formation size.

The formation of particles on catalyst thin film is very important for CNT growth because the uniformity of the catalyst thin film thickness is very crucial. This is because the surface roughness will affect the size of particles formation. The particle size will be smaller when the uniform thickness is successfully achieved. In order to control the uniformity of the thickness of the catalyst thin film, there are some parameters that needed to be controlled during the spin coating process. The parameters are rotation speed, process duration and spin time. By controlling this parameter, the uniformity of the catalyst thin film on iron catalyst can be controlled.

Heat treatment for the catalyst thin film is one of the most important processes to be done. The heat treatment process will help to develop the particles that consistent to the thickness of the catalyst thin film and due to that, the suitable temperature of heat treatment is needed.

1.3 Objective

i. To synthesis uniform thickness of iron nitrate catalyst thin film by controlling the spin coating parameter.

ii. To study the influence of heat treatment process and the particles formation.

1.4 Scope

This research will be based on several scopes to ensure that the project will not be distracted by other factors.

i. To achieved the first objective, the parameter and scope will cover on:
   - The preparation of solvent based on iron nitrate precursor.
   - The spin speed of the spin coating machine from 6500 rpm to 8000rpm.

ii. For the second objective, the scope covers are:
   - The annealing temperature is done on vacuum furnace.
   - The range of temperature for annealing treatment is from 350ºC to 500ºC

As for the characterization methods, both objectives were characterized by using field emission scanning electron microscopic (FESEM) and x-ray diffraction. (XRD)

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter will discuss on the fundamental of relation between parameter and the spin coating process to produce such uniform thickness of catalyst thin film. This chapter also covers the importance of heat treatment on the catalyst thin film for particles formation that is really important due to the fact that CNT growth is depending on the catalyst thin film. The needs of finding the right portion of parameters for catalyst thin film formation is very high demanding. Not forgotten, the heat treatment process is also a crucial part of the CNT growth because without the suitable temperature the particles will not fully form on the surface of the silicon substrate.

2.2 Solution process/ Sol-gel process

The sol-gel method was developed in the year of 1960s which principally due to the needs of production way in the nuclear industry. Sol-gel process is defined as construction of an oxide network through polycondensation responses of a molecular precursor in a liquid (Huang et al., 2001).

A sol is actually a dispersion of colloidal particles or polymer in solvent. The particles can be in a form of amorphous or crystalline, while a sol is a particle in a liquid. A sol disperses of the solid particles (> 0.1-1µm) in a liquid where only the Brownian motions dangle the particles (Huang et al., 2001).

A gel is a condition where both liquid and solid are dispersed into one and other, whereby it show a solid network having liquid components. A gel is comprises of a three dimensional continuous network, which surrounds by liquids. In a colloidal gel, the network is constructed from combination of colloidal particles. In the polymer gel, the particles have a polymeric structure sub-structure made by wholes of sub-colloidal particles.

2.2.1 Sol-gel processing method

The sol-gel method is a method that operates on a low temperature for producing material that is whichever fully not organic in nature or combination of organic and not organic. The condensation and hydrolysis that was created by the process resulting in reaction of organometallic compounds in alcoholic solutions that can give many benefits for the construction of coatings, including good control of the reaction of originator solutions. It also easy to control the compositional adjustments, customizable microstructure, easy to introducing many functional groups or summarizing sensing elements, relatively low annealing temperatures and the prospect of coating deposition on larger substrates, with simple and low-cost equipment. Within the past years, a number of developments in originator solutions, coating processes and apparatus have made the sol-gel technique even more widespread. The sol-gel process can be classified into two different routes depending on the nature of the precursor which are the precursor is an aqueous solution of an inorganic salt or a metal organic compound (Niederberger and Nicola 2009).

Several methods can be used to make sol-gel coatings with the sol-gel process as mention in Figure 2.1. Spin coating and dip coating are two basic techniques applied to deposit the sol gel coating on the substrate. Spin coating is one sided coating compared to dip coating; it can be done in both sites which is double sided coating. Both techniques are used to manufacture different coating on thin film.

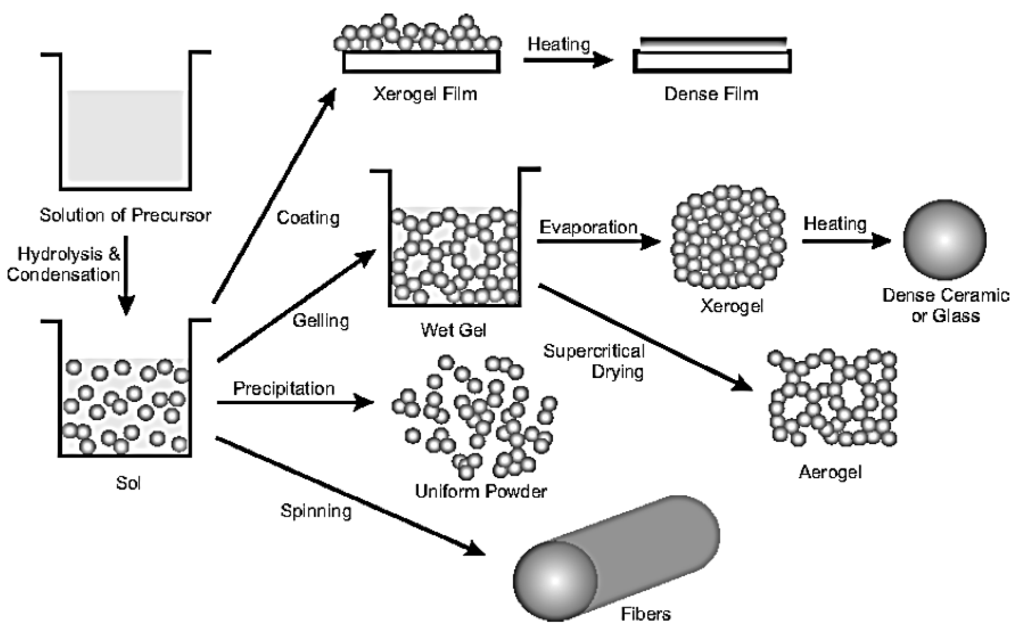

Figure 2.1: Sol-gel processing method. (Niederberger and Nicola 2009)

If the gel is dried by evaporation, then the capillary forces will result in shrinkage, the gel network will collapse, and a xerogel is formed. If drying is performed under supercritical conditions, the network structure may be retained and a gel with large pores may be formed.

2.2.2 Advantages of sol-gel process

As mentioned before, sol-gel process is a process that offers many advantages compared to other thin film deposition method. One of the main advantage sis it can produce thin bond-coating to provide excellent adhesion between the metallic substrate and the top coat. The list below is the additional advantages that can be offered by sol-gel technique:

i. Provide corrosion protection by its thick coating.

ii. It can easily shape materials into complex geometries in a gel state

iii. It can produce high purity products because the organo-metallic precursor of the desired ceramic oxides can be mixed, dissolved in a specified solvent and the composition can be highly controllable.

iv. It can have low temperature sintering capability, usually 200-600°C.

v. It can provide a simple, economic and effective method to produce high quality coatings.

2.2.3 Disadvantages of sol-gel process

Apart from its advantages, sol-gel processes still have some lacking due to some limitations such as high permeability, low wear resistance, week bonding and hard to control the porosity. In specific, maximum limit of the coating thickness is 0.5µm when it's have crack free properties is an crucial requirement (Olding et al., 2001). The organics trap with the thick coating is frequently happened and it will lead to failure during thermal process. The present sol-gel technique is very depending on its substrate, and the thermal expansion mismatch limits the wide application of sol-gel technique.

2.3 Spin coating thin film

Spin coating process is at this time the major method used to create uniform thin film of photosensitive organic materials with micrometers and nanometers thickness. The pioneer in the study of spin coating was accomplished with more than fifty years ago by Emil who deliberated the spreading of a thin film axisymmetric of the Newtonian fluids on a proposer rotating substrates with an angular speed (Sahu et al., 2009). In most cases, the polymeric coating material is applied in a solution form, where the solution vaporizes. Paint and pitch coating was the first the being studies using spin coating.

The spin coating process is extensively used in the manufacturing of integrated circuit, optical glass mirror, screen color television and magnetic disk function for storing data. Centrifugal force moving the liquids radiated outward. The surface tension and viscous force cause the thin residual film to be retained on the flat substrate surface. The thickness of the film can be reduced by the combination of both factors which are the evaporation and outward fluid flow.

There are several key stages classified from spin coating process which were the fluid dispense, spin up, stable fluid out flow, and final stages is evaporation dominated drying. Several parameters processing involved in the process of spinning are volume dispenses, final spinning speed, final thickness film, viscosity of the solution, concentration of the solution , spinning time and etc. By the used of different parameters, the thickness of the film and the spreading radius can be calculated. The formation of film process is mainly driven by the two free parameters which are the spin speed and viscosity. The thickness of the film produced has widely range and it easily accomplished by spin coating around 1 to 200 micrometers (Sahu et al., 2009).

2.3.1 Procedure of spin coating method

Deposition of thin films by spin-coating is a very simple and widely used technique to prepare films of uniform thickness of non-volatile materials initially found in liquid solution dissolved in a volatile solvent. The technique is particularly suitable to obtain thin films of conjugated polymers (Aguilar& Lopez, 2011) from their solutions in organic solvents or in liquids.

The physics of spin coating can be effectively modeled by dividing the whole process into four stages, which were the deposition stage, spin up stage, spin off stage and the evaporation of liquid. Usually, the first two stages commonly in sequel, but the spin off stage and the evaporation stage commonly overlap. The stage 3 (flow controlled) and stage 4 (evaporation controlled) are two stages that contribute most on the final thickness of thin film (Sahu et al., 2009).

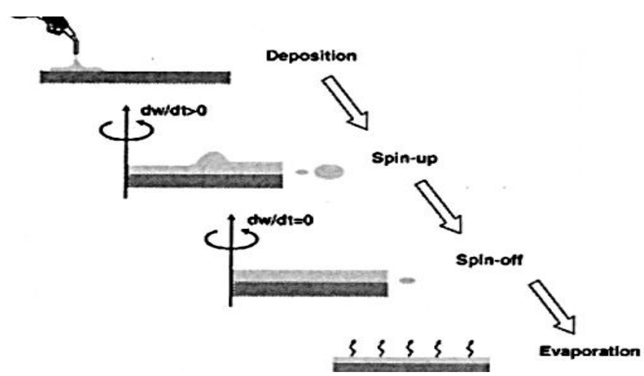

Figure 2.2: Spin coating processing sequence. (Sahu et al., 2009)

2.3.1.1 Deposition

At this stage, the solution was allowed to fall on the rotating substrates and the substrate is speed up to the desired speed. The spreading of the liquids happens due to the centrifugal force and resulting in reducing height towards the critical height. This is the stage where it transporting an excess of the liquids onto the substrate surface which it immediately covered or wetted. During this stage, deposition of liquid can be in many ways such as:

i. As a heavy rain that covers the whole disk.
ii. As a smacking at the center and the liquids will covered the entire disk by the means of spreading.
iii. As a nonstop stream at center and the liquid flowing all over the disk to cover with coating (Sahu et al., 2009).

2.3.1.2 Spin-up

The second stage of spin coating process is the substrate is speed up until it reaches its final desired speed. This is known as acceleration. During this stage, it commonly defined by the fluid removal aggressiveness from the rotational motion on its water surface. Due to the depth of initial fluid on the water surface, the present of spiral twisted might be found at this stage. This might be the result from the twisting motion caused by motion of inertia that the top of the fluid layer and at the same time, the water below keeps rotating in increasing speed. When, the liquid is thin enough, which it's completely co-rotating with the substrate, the difference between the thicknesses is gone. Finally, when the substrate reaches its desired speed and the thickness of the thin film is thin enough, the viscous shear drag the rotational acceleration balance.

2.3.1.3 Spin off

The next stage of spin coating process is when the substrate is rotating at a constant desired speed at a constant rate and the viscosity of the fluid control the thickness of the thin film. During this stage, it commonly defined by the thinning of steady fluid. Usually the fluid thinning is uniform, even though the solution is not in stable condition. The thickness is depending on the viscosity, surface tension, rotation rate and etc., there may be a small drop of coating thickness difference around the edge of the final wafer. If the fluid thickness is initially uniform across the wafer then the fluid thickness profile at any following time will also be uniformed.

2.3.1.4 Evaporation

An inert gas flow on top of the surface causing the functional liquids to vaporize that leads to super saturation process. The crystalline of salt catalyst is out uniformly. Due to the short time of evaporation (within few second), the crystal that form is in nanometer sized (Medhekar, 2004).

2.2.3 Advantages and disadvantages of spin coating thin film

There are many advantages offered by the spin coating process whereby the thin film thickness can be change easily by changing the spin speed of the spin coater or change the viscosity of the liquids. As compared with other coating techniques, there are too many parameters that need to be control leading to a more complex process

Other than that, spin coating process have the ability to produce a uniform thin film with a low cost production and the porting time is also fast. The effectiveness of this process can be enhanced by the studies to further understand the full process and parameters.

One of the main disadvantages of this process is the efficiency of material used. The process only utilizes around 2 to 5% material distributed on the substrate the rest of 98 to 95% were flung off.

2.4 Catalyst thin film

As we all know, the properties of the catalyst effects on the growth of the nanotubes. The formation of catalyst of catalyst thin film is very important for the CNT growth. There are many techniques used for developing catalyst thin film such as Chemical Vapor Deposition (CVD), Laser Ablation method and Arc-discharge technique in which have a huge lapping in there process because the manufacturing of catalyst cluster on flat surface is not completely controlled. Most of the techniques used including CVD do not give much control to the growth and the properties of the carbon nanotubes. The thickness of the catalyst of the thin film need to be control because the catalyst that deposited on the substrate is going to be used to grow the carbon nanotubes.

2.4.1 Catalyst thin film formation

The huge draw back in CNTs development is in the current technologies of carbon nanotubes. Efficient cost and the effectiveness of growth method are the main point for mass production of CNTs. To achieve the goal, many methods have been developed. Catalyst thin films have been prepared by a variety of techniques such as molecular beam epitaxy (MBE), RF magnetron sputtering, and pulsed laser deposition; spray pyrolysis, CVD and sol–gel process. The sol–gel process is one of the versatile methods to prepare thin film-supported nano-sized particles without complicated instruments such as CVD. It is simple, cheap, and has a general advantage of large area deposition and uniformity of the films thickness (Raoufi & Raoufi, 2008).

2.4.2 Particle formation on catalyst thin film

The formation of catalyst particles with various size variations is observed in order to understand effect of various types of parameters with the formation of particles. For the purpose of analysis, the distribution of uniform catalyst on the entire surface of substrate, it is helpful to compared between the average thin film thicknesses with the surface roughness. It is likely for the catalyst thin film continuous when the roughness is smaller than the thickness.

On the other hand, if the catalyst average value thickness is lower than the roughness value, separate particles formation is possible. Most of the cases show that small elongated catalyst particles can be detected at the end of tip of tubes. This indicates that the growth mechanism is tip grow (Moshkalyov et al., 2004). The density of the nanotubes be determined the treatment on the catalyst before the synthesis and on the delay between the film deposition and the process. The growth process and the nanotube nucleation depend strongly on the catalyst film thickness and on the conditions of the treatment on surface before growth. A good result is a long straight carbon nanotube with diameter of 10 nm smal or less was obtained at high growth temperatures.

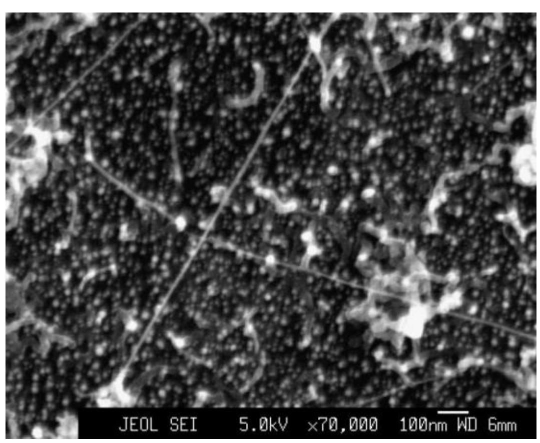

Figure 2.3: SEM image of nanotubes grown by thermal CVD, H2/CH4 = 400/100 sccm, 900 8C, 20 min, 1 nm Ni film. (Materials Science and Engineering B 112 ,2004)

2.4.3 Catalyst thin film through solution process

As discussed before, the simplicity of the spin coating process for depositing the catalyst on the flat surface such as silica (SiO_2) and alumina single crystal (Al_2O_3) Spin coating process is employed in order to deposited a fine layer functional solution on the flat surface. The usage flat surface support which consists of SiO_2 and AL_2O_3 giive a huge benefits with respect of sensitive spectroscopic surface methods (Medhekar, 2004). One of the benefits is the catalyst is ready and available for analysis. Flat surface support also enables the use of methods such as tunneling microscopy (STM) and atomic force microscopy (AFM). The transportation of heat transfer and mass to the surface of the catalyst from the mixture of reaction are commonly gone the result is fairly easy to interprets

The used of catalyst for CNTs growth which basically been supported on the alumina or silica which consist of porous catalyst support. In this system, the catalyst distribution cluster and the characteristic made it difficult by the incapability to control the cluster nature that contributes to the formation on CNTs. Other than that, the control of catalyst size is very difficult because of few factors such as speed and the concentration of the solution.

2.4.4 Parameter that influence the catalyst thin film and particles formation

Spin coating parameters and heat treatment proses are always be the main Figures of the whole process. All around this world, the researchers try hard to find the right portion and also the balance in the parameter of spin coating and heat treatment to produce uniform catalyst thickness that lead to the growth of CNTs.

2.4.4.1 Effect on concentration of solution

Concentration of the solution is one of the most important parameter in the formation of the catalyst thin film. This is mainly because the thickness of the catalyst thin film can be controlled by adjusting the concentration of the solution. The density of CNT thin films was controlled by the concentration of catalyst in the solution (Sangwan et al, 2010). Other than that, the higher number of concentration of salt, more amount of solid solution present to crystalize. The formation of more than one cluster happened when the material is concentrated. It can be said that, the particle density and also the particle size increase with increasing concentration of crystal salt as mention in Figure 2.4.

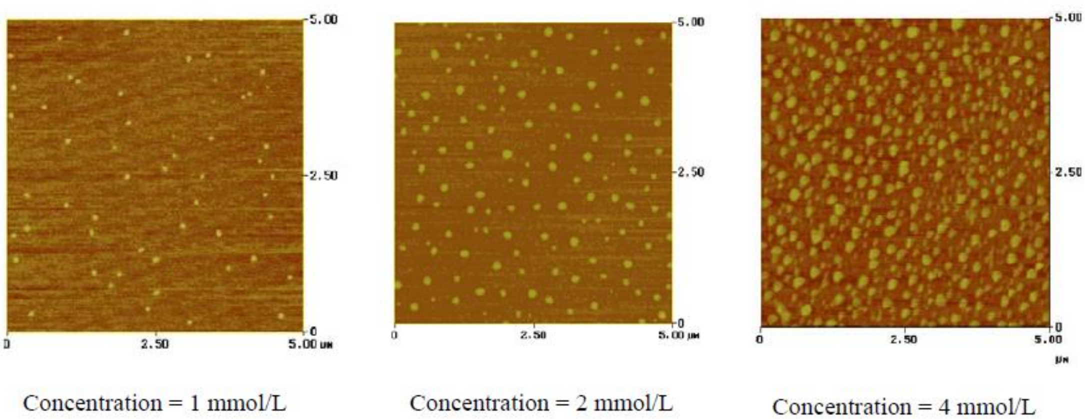

Figure 2.4: AFM images on different concentration prove that high concentration will increase the thickness of the catalyst thin film. (Medhekar, 2004)

2.4.4.2 Effect on speed of spin coating

Speed of the spin coating machine also plays important role in developing the characteristic of the catalyst thin film formation. The speed contributes in term of distributing the salt solution onto the surface of the substrate. When the spin speed increased, the acting centrifugal force on the catalyst salt solution coated on the surface of the substrate is increases. The thickness of the catalyst thin film that stay on the substrate surface due to the capillary force that influence leads to the reduce amount of salt solution (Medhekar, 2004). The quantity of deposited solid on the surface after the evaporation of the liquids solution is less and is revealed in the shape of fine fize of particle on the surface as shown in Figure 2.5.

6000 rpm	7000 rpm	8000 rpm
500°C	500°C	500°C
3.23 nm	2.50 nm	1.77 nm

Figure 2.5: AFM images show that the particle size and density will decrease at high speed of spin coated thin film. (Wei et al., 2009)

2.4.4.3 Effect of temperature on catalyst particle

The stability and the uniformity of the cluster play an important role in formation of CNTs and also their properties. Cluster combines at high temperature of oxidation or reduction and the reaction of the salt are treated to gain the catalyst metal (Medhekar, 2004). With the suitable temperature, the large agglomeration of iron salt can be prevented. There are two ways to prevent the cluster to agglomerates which are reduction and oxidation.

The reaction process is done by using metal salt that have large molecule to prevent the cluster approaching close to one and other during the reaction process and reduction.