UNIVERSITI TEKNIKAL MALAYSIA MELAKA (UTeM)

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

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

by

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DECLARATION

I hereby, declared this report entitled 'Influence of Solution Process Parameter to Cobalt Catalyst Thin Film and Particle Formation' is the results of my own research except as cited in references.

Signature	:	……
Author's Name	:	Nik Mohamad Azren Bin Mohd Zubir
Date	:	23th May 2014

APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of UTeM as a partial fulfillment to the requirements for the degree of Bachelor of Manufacturing Engineering (Engineering Materials) (Hons.). The member of the supervisory is as follow:

……..

(Dr. Mohd Asyadi Azam Bin Mohd Abid)

ABSTRACT

This report study about the influence of solution process parameter to cobalt catalyst thin film and particle formation. Cobalt is selected as the choice of material due to its excellent performance to produce thin film with thickness below 100 nm. There are two phase involved during thin film preparation which are spin coating and annealing. Using spin coating process the thickness of the film can be manipulated by changing its spin speed or altering solution viscosity. In annealing process the thin film is heat treated in order to produce uniform size of cobalt particles in thin film. Furthermore after completing these two phase in solution process, the cobalt thin film will undergo characterization for surface morphology and elemental confirmation that can be done by using Field Emission Scanning Electron Microscopy (FE-SEM) and Xray Diffraction (XRD).The result shows that increasing spin speed reduces the Co film thickness and increasing temperature of heat treatment result in larger particle formation. This can be concluded that particle and thin film formation was successfully done by using solution process.

ABSTRAK

Laporan ini mengkaji mengenai pengaruh parameter proses larutan keatas pembentukan partikel untuk kobalt sebagai pemangkin filem nipis. Cobalt telah dijadikan sebagai bahan pilihan disebabkan oleh prestasinya yang cemerlang dalam menghasilkan filem nipis dengan ketebalan kurang daripada 100 nm. Terdapat dua fasa yang terlibat semasa penyediaan filem nipis iaitu lapisan putaran dan sepuh lindap. Menggunakan proses salutan spin ketebalan filem itu boleh dimanipulasi dengan menukar kelajuan putaran atau mengubah kelikatan larutan. Dalam proses penyepuh lindapan filem nipis dikenakan rawatan haba untuk menghasilkan saiz zarah kobalt yang seragam dalam filem nipis. Tambahan pula selepas menamatkan kedua-dua fasa dalam proses larutan, filem kobalt nipis akan menjalani pencirian untuk morfologi permukaan dan pengesahan unsur. ia boleh dilakukan dengan menggunakan Mikroskop Transmisi Elektron (TEM), Field Mikroskop Pelepasan Imbasan Elektron (FE SEM) dan Difraksi Xray (XRD). Hasilnya menunjukkan bahawa peningkatan kelajuan putaran mengurangkan ketebalan filem Co dan suhu yang semakin meningkat hasil rawatan haba dalam pembentukan zarah yang lebih besar. Ini boleh membuat kesimpulan bahawa zarah dan filem nipis pembentukan telah berjaya dilakukan dengan menggunakan proses penyelesaian.

DEDICATION

To my parents and family members for their continuous support throughout my study.
To my supervisor and postgraduate student for their advice and guidance in completing this research.

To all my friends for their continuous support and help in completing this report.

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°C	-	Celcius
µL	-	micro litre
$Al(NO_3)$	-	Aluminium Nitride
$Al(OC_4H_9)_3$	-	Aluminium s-Btoxide
Bhd.	-	Berhad
CNT	-	Carbon nanotube
Co	-	Cobalt
Co_4O_3	-	Cobalt Oxide
CoFe	-	Cobalt Iron
CVD	-	Chemical Vapor Deposition
FE-SEM	-	Field Emission Scanning Electron Microscopy
ISFM	-	International Symposium Functional Material
ITEX	-	Invention Innovation and Technology Exhibition
kV	-	kilo Voltage
MWCNT	-	Multi Walled Carbon nanotube
nm	-	nanometer
PtMn	-	Platinum Manganese
PVD	-	Physical Vapor Deposition
RFID	-	Radio Frequency Identification
rpm	-	Revolution Per Minutes
s	-	Second
Sdn.	-	Sendirian
SiGe	-	Silicon Germanium
SWCNT	-	Single -Walled Carbon nanotube
TEOS	-	Tetraethyl Orthosilicate
TiW	-	Titanium Tungsten
UTeM	-	Universiti Teknikal Malaysia Melaka
VLS	-	Vapor Liquid Solution

XRD - Xray Diffraction

CHAPTER 1
INTRODUCTION

The purpose of this project is to study the parameter in the solution process which can affect the thin film formation . Cobalt is used as the material for the thin film that acted as catalyst for CNT growth. This chapter described about the relevance and background to the project, it discussed about the importance of thin film towards CNT growth. Several objectives and scope that needed to be achieved in this project is briefly explained .

1.1 Background

The development in nanotechnology has led to the growth of carbon nanotubes (CNTs). The impacts on CNT growth provide huge potential in electric and electrical industry like photovoltaics, sensors, semiconductor devices, displays, and conductor and so on. Catalyst nanoparticles are essential in order to grow CNT. These catalyst nanoparticles can be obtained from thin film after heat treatment process. However controlling the catalyst formation enable the improvement in the CNT growth. Thin film consists of thin layer of resistor material deposited on the surface of substrate and followed by a thin layer of metal. Thin film is formed mostly by deposition, either physical or chemical method. It can also be amorphous polycrystalline or single crystalline. Therefore solution process is a promising technique to produce uniform, ultrathin film with thickness of nanometer. However, the production of these ultrathin films is still undiscovered and under research. In many optoelectronic applications, it is desirable to get the thickness of the thin film below 200 nm with good quality surface. Furthermore, solution process technique have been given high

attention due to its simple deposition procedure, easy control of chemical components and low cost preparation to obtain high quality thin films (Shivaraj *et al*., 2013).

Spin coating technique is one of the methods involved in solution process technique to deposit thin film. The properties of thin film deposited by spin coating technique are influenced by several parameters such as pre coating, coating, and post coating parameter (Shivaraj., 2013). Spin coating is consists of several stages which are deposition, spin up, spin off and evaporation. During spin coating, A fluid resin is deposited at the centre substrate and spinning the substrate at high speed. Centrifugal force will cause the resin to spread over the planar on the substrate and leaving a thin film of resin on the surface. Final uniform thickness is influenced by several parameters such as spinning speed, spinning duration, solvent concentration, volume of the resin, drying rate etc.

1.2 Problem Statement

In CNTs production, the application of physical vapour deposition (PVD) method is widely used to produce thin film which is a layer that contains catalyst nanoparticles. The catalyst is acted like seeds that enable the growth of CNT. Unfortunately, the needs of large vacuum device in PVD has led to inefficiency usage of energy and material in manufacturing process and consumes higher production cost. In PVD large amount of heat is required which it needs the skilful operator. Furthermore the rate of coating is slow even though it provide good particle formation thin film thickness.

Meanwhile, solution process is one of the method to produce thin film since it is lower cost, large deposition, simple equipment, easy to operate and can be done in normal atmosphere compared to PVD method. Since the thin film is correlated with CNT growth, uniformity and good particle distribution are the aspects that are very important because it can affect the efficiency of the catalyst to grow CNT. Therefore solution process is chosen since it provides good control of uniform thickness in thin

film and particle formation through spin coating process and heat treatment. However, there are still few studies on solution process to achieve optimum parameter that can be selected in order to provide good thin film formation for CNT growth. In order to achieve optimum parameter, consistency and repeatability of the result is required.

1.3 Objective

The main purpose for this project is to produce and characterize the cobalt catalyst thin film. In order to reach the goals, the research is conducted based on several aims which are:

1. To investigate the effect of spin coating speed parameter to produce uniform thickness of cobalt catalyst thin film.
2. To study the influence of heat treatment of thin film for Co nanoparticles formation.

1.4 Scope

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

To achieve the first objective ,the parameter and scope will be covered on :

1. Cobalt acetate tetrahydrate and ethanol is used to form precursor solution cobalt acetate precursor.
2. The spin speed of the spin coating machine from 6500 rpm to 8000 rpm.

For the second objective, the scope covered is :

1. The heat treatment is done on vacuum furnace for 10 minutes for all temperature parameter.
2. The range of heat treatment temperature range from 450 $^{\circ}$C to 600 $^{\circ}$C.

Both spin coater and CVD furnace are available in the UTeM Polymer Laboratory. Characterization on surface morphology is done using field emission scanning electron microscopy (FE-SEM) at High Tech Instrument, Puchong while characterization for elemental conformation using x-ray diffraction is done in UTeM Polymer Laboratory.

CHAPTER 2
LITERATURE REVIEW

The ultimate goal for this project is to optimize the thin film formation that deals great potential in CNT growth technology, it is better to replace high energy consuming PVD to the solution process which can be conducted in a simple way in ambient environment. This chapter provides background information and history about CNT. Information on particle synthesis and its link to the catalytic growth on particles is also provided. Moreover theory and information about particles and particle synthesis is discussed and elaborated. Furthermore, several types of thin film deposition that is often from the previous research. Finally influence of parameter of spin coating and annealing are also described.

2.1 Carbon Nanotubes (CNTs)

CNTs were first discovered about 30 years ago. However during that time CNTs are not appreaciated.Then, in 1950s, Rogwer Bacon discovered a new strange type of carbon. He found that hollow tubes of carbon consist of graphite layers separated in the same spacing as the planar layer of the graphite. later in 1970s Morinobu Endo found that there are some tube consist of a single layer roll of graphite. In 1991 Sumio Ijima found an extremely thin needle like material during examination of carbon material under electron microscope. Later he named the strucure as CNTs.

CNTs is known as a structure of long sheet that rolled into a tube with their edges joined to form a seamless cylinder and place a cap on the open end of the tube. The CNTs can posses metallic or semiconductor ability depending on their geometric

structure such as diameter and the chirality. The tube can be made into Single-Walled Carbon Nanotube (SWCNT) and Multi-Walled Carbon Nanotube (MWCNT). SWCNT is the tube that is made out of single layer carbon atom. The CNTs can posses metallic or semiconductor ability depending on their geometric structure such as diameter and the chirality. Multi-walled Carbon Nanotube (MWCNT) consists of layers of carbon sheets that wrapped one another. Several method have known in order to produce CNTs such as laser ablation, arc dicharge deposition and chemical vapor deposition.

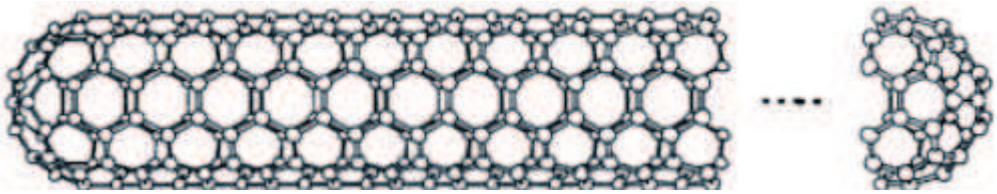

Figure 2.1: Carbon nanotube structure

2.2 Thin Film

A thin film can be known as a layer of material ranging from nanometer to several micrometer in thickness. Diamond-like and Teflon-like films offer special properties, as do various alloys like PtMn, TiW, SiGe and CoFe (Fransilla., 2010). Thin film possess very unique characteristic that is different from bulk material since their properties depend on several parameter and fabrication technique. Deposition technique is used to fabricate and control the layer of thickness for thin film and the material tend to have different properties when they are in the form of thin film.

2.2.1 Thin Film Deposition Technique

Physical Vapour Deposition (PVD) is a technique that forms thin layer of chemicals is applied on substrates which are later vaporized with heat in a vacuum chamber. It is suitable to fabricate films with thicknesses in the range of a few nanometres to thousands of nanometres film . Besides that, production of multilayer coatings, graded composition deposits, very thick deposits and free standing structures are possible when using PVD.

Furthermore, the advantages of PVD are it can provide high deposition rate with less surface damage of thin film and produce excellent purity of the film due to vacuum mechanism (Maltone, 2009). However it is difficult to control film composition while maintaining uniform film thickness when using vacuum evaporation method .There are three types of processing method in PVD which are vacuum evaporation, sputtering deposition and ion plating .

The solution process also known as sol gel process is a wet chemical technique which is known as Chemical Solution Deposition. A colloid can be defined as suspension which the dispersed phase having range size from one to one thousand nanometer that neglect gravitational force. A sol is a colloidal suspension of solid in liquid that can move freely. A gel has three dimensional continuous network whereby the particle in the solid phase are fixed and cannot move freely, In sol gel the compound is dissolved in liquid to form solid back in controlled manner.This method prevent problem of co precipitation which causes inhomogeneous formation.

2.3 Spin Coating

Spin coating is one of the techniques in sol gel process. It has been used for several decades for the application of thin films. It is a typical process that involves depositing a small puddle of a fluid resin onto the centre of a substrate and then spinning the substrate at high speed (Taleb *et al*., 2009). The spin coating technique is a fast and easy method to generate thin film out of the solutions (Aguilar *et al*., 2011). It is also able to apply uniform thin films to flat substrates. In this process a solution will be deposited on the substrate and rotated at high speed in order to spread the fluid by centrifugal force.

2.3.1 Working Principle

Based on Figure 2.1 , the mechanism of the spin can be divided into four stages which are deposition, spin-up, spin-off and evaporation of solvent. During the spin-off stage and evaporation stage, they are usually overlapped since both run simultaneously (Sahu et al., 2009).

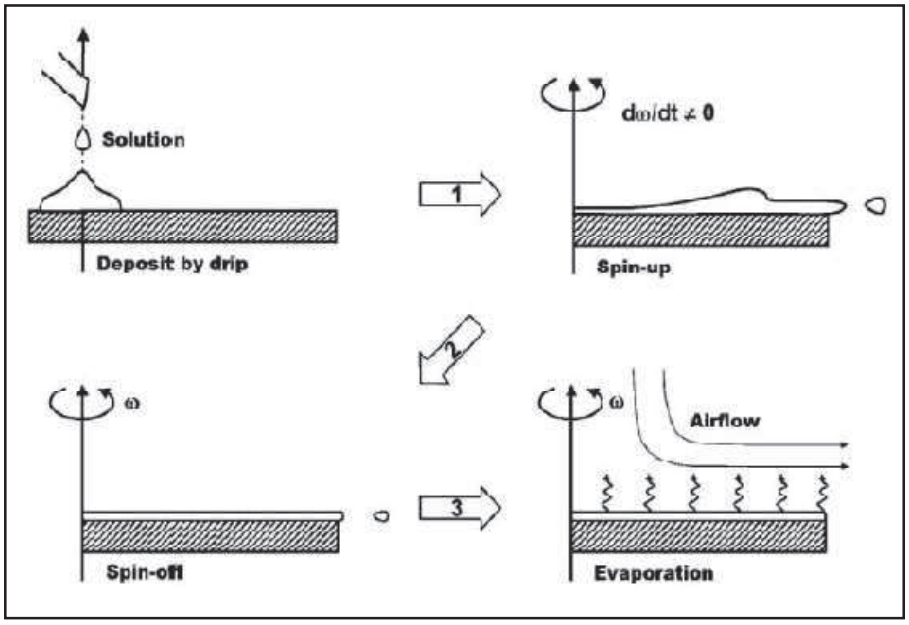

Figure 2.2: Overall stages in spin coating process mechanism (source: Aguilar *et al*.,2011)