DEPOSITION AND CHARACTERISATION OF TiO_2 LAYER USING MAGNETRON SPUTTERING DEPOSITION TECHNIQUE

RIYAZ AHMAD BIN MOHAMED ALI

A thesis submitted in
fulfillment of the requirement for the award of the
Degree of Master of Electrical Engineering

Faculty of Electrical and Electronic Engineering
Universiti Tun Hussein Onn Malaysia

SEPTEMBER, 2013

ABSTRACT

Titanium dioxide (TiO_2) film is one of the promising candidate materials that often used in various applications such as photo – sensor, ultra – violet (UV) protection and solar cell applications. In this study, TiO_2 thin film was prepared by a RF reactive magnetron sputtering system using Titanium (Ti) target as the starting material. Results using Optical Emission Spectroscopy (OES) and Langmuir Probe equipment show that density plasma distribution of Ti, Ar, Ar^+ and O atom changes with respect to discharge power, working pressure (WP) and environment gas ratio. Observation on the atomic lines of Ti I and Ar I in pure Argon environment was found increased as the discharge power and working pressure increased. Emission line intensity of Ar^+ ions with wavelength of 443.02 nm shows significant increase as the discharge power increases. Increase in Ar^+ ion population has contributed in increase of atomic Ti released inside the system. Influence of O_2 gas flow in reactive magnetron sputtering is very critical during the formation of TiO_2. Significant change in emission response of Ti and O lines suggests TiO_2 film starts to form over critical ratio of 7% ratio of O_2/ (Ar + O_2). Further investigation using X - ray diffraction (XRD) shows that TiO_2 film has been formed with anatase crystallite behavior. In addition, Atomic Force Microscope (AFM) result shows that the TiO_2 particles size increases as the working pressure increase inside the deposition chamber. Smooth film with roughness less than 1.6 nm was also observed. High transmittance (>70%) in the visible region can be generally observed using Ultraviolet – Visible spectroscopy (UV –Vis). Direct optical band gap for TiO_2 thin deposited at working pressure of 5m, 10m, 15m, 20m, 30m and 40 mTorr was found 3.99, 3.38, 3.39, 3.43, 3.24 and 2.96 eV respectively. Therefore, by controlling those plasma properties in magnetron sputtering system, a good high quality TiO_2 film layer can be formed. This is important in order to optimize TiO_2 thin film for solar cell application.

ABSTRAK

Titanium dioxide (TiO_2) adalah suatu bahan yang sering menjadi bahan utama dalam pelbagai aplikasi filem nipis seperti pengesan fotonik, pelindung sinar UV dan sel suria. Di dalam kajian ini, bahan film nipis berasaskan TiO_2 telah disediakan menggunakan bahan Titanium sebagai permulaan dengan teknik *RF* percikkan bermagnet. Taburan ketumpatan atom Ti, Ar, Ar^+ and O pada bebola plasma telah diserap mengunakkan perkakasan *Optical Emission Espectroscopy* (*OES)* dan *Langmuir probe*. Beberapa jenis parameter seperti bekalan kuasa, tekanan gas didalam ruang penyaluran dan nisbah gas telah disimulasi dan direkodkan. Kajian pada Ti I dan Ar I atom menunjukkan kadar naik selaras dengan penambahan bekalan kuasa dan tekanan gas kedalam ruang penyaluran. Kadar ion Ar^+ pada lambda 443.02 nm menunjukkan kadar naik selaras dengan penambahan bekalan kuasa. Didapati kadar penambahan Ar^+ turut memberi sumbangan dalam peningkatan atom Ti. Kadar nisbah gas oksigen agak penting dalam pembentukkan molekul TiO_2. Kajian menunjukkan dalam keadaan pesekitaran O_2 / Ar + O_2, TiO_2 telah mula membentuk selepas nisbah 7%. Keputusan XRD berjaya menunjukkan film TiO_2 mempunyai bentuk kristal *anatase* pada suhu 400 °C. Keputusan AFM menunjukkan size zarah TiO_2 yang dihasilkan mengalami penambahan diameter seiring dengan penambahan tekanan gas didalam ruang pericikan. Didapati filem nipis yang licin dengan tahap kekasaran 1.6 nm telah berjaya diperhatikan. Kadar penembusan cahaya setinggi 70% telah direkodkan dengan menggunakan UV- Vis. Rintangan tenaga didapati meningkat daripada 3.99, 3.38, 3.39, 3.43, 3.24 and 2.96 eV untuk sampel tekanan 5m, 10m, 15m, 20m, 30m and 40 mTorr. Tahap ringtangan turut menunjukkan penambahan drastik selangkah dengan peningkatan ketebalan film TiO_2 yang dihasilkan. Peubahan ini menunjukkan kolaborasi yang baik antara sifat plasma yang diwujudkan dan film nipis yang dihasilkan. Dengan mengawal selia parameter plasma ketika proses penyaluran, suatu filem pelindung TiO_2 yang baik boleh dihasilkan. Ini adalah penting untuk digunakan bersama aplikasi DSSC.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

$\theta°$	-	2theta degree
Al_2O_3	-	Aluminium Oxide
Ar I	-	Atomic line Argon
O I	-	Atomic line Oxygen
Ti I	-	Atomic line Titanium
Cu	-	Copper
m^{-3}	-	Cubic meter
z	-	Distance between Target and substrate
η	-	Efficiency
T_e	-	Electron Temperature
eV	-	Electron volt
e^-	-	Electrons
Ar^*	-	Excited short – live Argon radicals
Ar	-	Gas Argon
N_2	-	Gas Nitrogen
O_2	-	Gas Oxygen
“	-	Inches
Ar^+	-	Ion Argon
n_e	-	Ion density
Ti^+	-	Ion Titanium
kV	-	Kilo Volt
Ar^M	-	Long – live Argon metastable
P_{max}	-	Maximum power
Ω/cm	-	Ohm per centimeter
W	-	Power
k_i^e	-	Rate of coefficient

LIST OF ABBREVIATIONS

AFM	-	Atomic Force Microscope
AES	-	Auger Electron Spectroscopy
CVD	-	Chemical Vapour Deposition
I – V	-	Current – voltage
DI	-	Deionized water
DC	-	Direct Current
N719 dye	-	Dye Ruthenium complexes
DSSC	-	Dye Sensitized Solar Cell
FESEM	-	Field Emission Electron Scanning Microscope
ITO	-	Indium doped Tin Oxide
a.u.	-	Intensity in absorbance / arbitrary unit
LP	-	Langmuir Probe
L/min	-	Liters per minute
MFC	-	Mass gas flow controller
MHz	-	Mega Hertz
MC	-	Metal contact
MG	-	Microscope glass
ms	-	Millisecond
mT	-	Millitesla
mTorr	-	Millitorr
$Ar + O_2$	-	Mixture of Argon gas and Oxygen gas
nm	-	Nanometer
OES	-	Optical Emission Spectroscopy
hv	-	Photon emission
PVD	-	Physical Vapour Deposition
Pt	-	Platinum
rf	-	Radio frequency
RBS	-	Rutherford Backscattering Spectroscopy
SEM	-	Scanning Electron Microscope
Si	-	Silicon

CHAPTER 1

INTRODUCTION

1.1 Introduction

Thin film technology has become a sophisticated and advanced technology used in various fields. Surface modification engineering using thin film technology represents a new class of materials in nano – scale which exhibit functional alteration in atomic, electrical, mechanical, optical, thermal and magnetic properties through the variation in the material composition, doping, multilayer films and lithographic patterning (Smith, 1995). The custom patterned film coating is used widely in various applications such as sensors, batteries, optical instrument, ceramics, solar cell, microwave communication, military and others. Such application highly depends on thin film properties such as type of material, particle grain size, density, particle adhesion, porosity, film thickness, film crystality, conductivity, topography and morphology, hardness, magnetic and composition (Mattox, 1998). Manipulation of these film properties up to certain criteria will enhance the overall performance according to the application needed.

Thin film deposition can be derived as an act of applying a layer (film) onto a substrate surface resulting new properties response emit from the existing bulk material (substrate). Advance fabrication techniques are designed to manipulate atomistic film deposition process to form preferable thin film layer on a substrate. Magnetron sputtering is one of the most common physical vapour deposition (PVD) techniques that used to deposit high quality and uniform thin film. The sputtering process involves the bombardment of high energy plasma ions on the surface of sputtering metal, which cause to dislodge a physical target atom to vaporise and then condense into a thin film of the target material (Mahan, 2000). The advantage of the

sputtering process includes high deposition rate, low substrate temperature, good surface flatness, transparency and dense layer formation (Ki Hyun, Choi, & Lee, 1997).

Titanium dioxide (TiO_2) is one of widely investigated transition metal oxide by many researchers in the world. The TiO_2 material can occur in nature mineral known as anatase, rutile and bookite catalytic phase. Generally, the TiO_2 material has a low density, high specific surface areas and performs good photocatalytic activities (Yu, Fan, & Cheng, 2011). The respective TiO_2 material are then fabricated using sophisticated technique to form TiO_2 thin film to be used extensively in various optical device thin film applications due to its attractive optical transmittance properties, good refractive index and excellent stability in adverse environments (Senthilkumar, Jayachandran, & Sanjeeviraja, 2010). These significant properties have led the TiO_2 thin film to be used in broad applications, such as the dye sensitized solar cell (DSSC), gas sensor and dielectric applications.

A high numbers of research are being carried out lately to study the sputtering conditions to enhance the thin film application performance. Study shows that TiO_2 thin film quality using magnetron sputtering technique is highly depended on critical parameters such as oxygen partial pressure, substrate type, discharge power, working pressure, substrate temperature and evaporation rate (Abdullah, Ismail, Mamat, Musa, & Rusop, 2013; Leprince-Wang & Yu-Zhang, 2001; Senthilkumar et al., 2010). By controlling these dependence parameters, the produced film properties can be alter to suit any needed application (Senthilkumar et al., 2010).

Further study on TiO_2 deposition using magnetron sputtering technique is needed to enhance the understanding of compound formation and quality of TiO_2 thin film produced. This includes the study on the plasma environment formed inside the magnetron sputtering where it will enhance the basic understanding of radical formation during the fabrication process. Study on the morphology, optical and electrical properties of produced TiO_2 thin film is crucial to be used as passivation layer in DSSC application to enhance its overall efficiency.

1.2 Background of Study

Various types of pure metal, ceramic oxides and composition thin film can be grown with high rate of repeatability and reliability using sputtering technique. TiO_2 thin film is one of the promising candidate materials that often used in various applications such as photo – sensor, ultra – violet (UV) protection and solar cell applications.

The DSSC has huge expectation to be used as future clean energy at lower production cost compared to conventional silicon solar cell (Zalas, Walkowiak, & Schroeder, 2011). There are four importance principle arrangements of the DSSC film, from top to bottom, the transparent conductive oxides (TCO)/TiO_2 layer, the TiO_2 layer/dye, dye/ redox electrolyte and the redox electrolyte/counter electrode. By arranging in such sophisticated layer arrangement manner, the DSSC start to function under present of sun light.

Study to enhance the overall DSSC efficiency value and cell durability has become world research agenda with highest lab-scale reported value of 12.3% efficiency (Yella et al., 2011). There are numerous approach method has been studied by many researcher in the world to increase the DSSC efficiency performance such as by controlling the morphology and particle size of the mesoporous of TiO_2 film (Ito, Kitamura, Wada, & Yanagida, 2003; Yu et al., 2011), prevent the recombination rate at the interfaces (S.-S. Kim, Yum, & Sung, 2005), developing new composition of dye (Ferrere & Gregg, 1998), thermal – resistance TCO (Kawashima et al., 2004), and improved electrolytes (Kusama & Arakawa, 2004). However, despite of the research work and effort contributed, studies on the interfacial contact between the mesoporous TiO_2 and TCO are limited (Ahn, Kang, Lee, & Kang, 2007). This study is crucial to understand the effect of interfacial contact between the film layers in DSSC in aiming to enhance its efficiency and durability of the solar cell.

Study shows that, high porous TiO_2 film is one of most common and essential approach used in DSSC to increase number of dye embed with the surface of TiO_2 oxide metal to boost the overall photoabsorbtion process in a cell (Yu et al., 2011).

Though this method, the particle size will be altered to form porous material that can hold a higher number of embed dye on this TiO_2 particle surface. However, the highly porous arrangement of TiO_2 layer may introduce an electrical short between liquid redox electrolyte and the TCO layer interface causing limited efficiency conversion (Jin, Kim, Kim, Jang, & Choi, 2012). From this study, it is clear that a unidirectional charge flow with no electron leakage between the films interface is the essential key to obtain higher energy conversion efficiency. To minimize this electron leakage phenomena, a compact TiO_2 passivation layer was suggested to be used between the TCO layer and mesoporous TiO_2 layer to prevent any back transfer of electrons due to direct contact in any DSSCs (Jin et al., 2012; Karthikeyan, Thelakkat, & Willert-Porada, 2006).

Study also shows that, this TiO_2 thin film with anatase catalytic behavior exhibits lower rates of recombination compared to rutile catalytic phase with good hole trapping properties (Hurum, Agrios, Gray, Rajh, & Thurnauer, 2003). In addition, anatase shows better photochemical properties compared to rutile phase in with higher surface adsorption capacity. High quality compact TiO_2 thin film with anatase catalytic phase is vital to be used as passivation layer in DSSC to increase the overall cell efficiency (Senthilkumar et al., 2010; Sung & Kim, 2007).

Few studies have been reported that sputtering system was used to fabricate a compact and dense TiO_2 thin film. A study reported by Jin et. al., the TiO_2 layer fabricated at 5m Torr working pressure is able to increase the overall efficiency up to 1.4% higher than existing without any passivation layer at a value of 3.2% (Jin et al., 2012). This breakthrough has further studied using various sputtering time of 1 hour, 3 hour and 5 hour and reveal that as the deposition time increase, the DSSC photovoltaic performance decrease of 4.8%, 4.6% and 4.2%, respectively. Another similar study on the effect of TiO_2 compact thin film thickness over DSSC performance, as reported by (Jeong & Kim, 2011) has disclosed that as thickness increases from without TiO_2 thin film layer, 10 nm, 20 nm and 50 nm, the power conversion efficiency has increased from 3.8%, 4.18%, 4.20% and highest at 4.42%, respectively. As the thickness increase up to 100 nm, the efficiency of the DSSC shows some drop until 4.13%. It is also clearly stated that in both referred study

paper, TiO_2 ceramic has been used as sputter source target during the growth of TiO_2 thin film.

Most of the study shows that TiO_2 ceramic as being used as sputter target. This type of target is usually limited, costly and fragile. Several independent papers have been suggested that TiO_2 can be prepared via sputtering technique using pure Titanium target with an aid of oxygen gas (Chen et al., 2008; Okimura, 2001; Senthilkumar et al., 2010). Study done by (Takamura, Abe, & Sasaki, 2004) shows the influence of oxygen gas ratio over argon gas is critical to form TiO_2 particles before sputter as thin film. Sufficient amount of oxygen gas flow into the sputtering chamber is needed before any TiO_2 particle formation can happen. It is also reported that TiO_2 particle will start to form above critical ratio of 7% oxygen flow (Takamura et al., 2004). The deposition rate is observed decrease drastically after this ratio value due to increase in target poisoning effect. In additional, study by Senthilkumar et al. shows that, anatase catalytic phase with behavior is possible to be form using pure Titanium target. This has been confirmed by the detection of characteristics peaks at $2\theta = 25.24°$ (plane 101) and $2\theta = 55.16°$ (plane 211).

Observation of atoms and ions radical species is possible using OES technique. Study by (Chen et al., 2008) shows that several strong emission lines of Ti, Ti^+, Ar, Ar^+, O and O^- are can be observed and recorded as the sputtering conditions are changed. Typical strong lines of Ti are observed at wavelength 365.1 nm and O at 777.2 nm. As the oxygen gas ratio was increased from 0% to 25%, the production of Ti emission was clearly reduced slowly then become completely undetected after passing 21% ratio. As the oxygen flow ratio was increased slowly from 0% to 25%, the emission of O becomes traceable after 12% ratio. The report suggested that under limited O_2 gas (below 12%) supply, the oxygen flux has been captured by the highly reactive Ti causing oxygen signal remain at background level (undetected). Similar present changes of O atoms at 777.19 nm are also observed and reported by (Belkind, Zhu, Lopez, & Becker, 2006). However, Ti^+ emission lines shows some difficulties to be detected, since this ion tend to merge with the spectrum causing untraceable with low spectroscopy resolution (Sirghi, Aoki, & Hatanaka, 2004).

1.3 Problem Statements

As mention previously, the dye sensitized solar cell (DSSC) has huge expectation to be used as a future new clean energy generator. Inexpensive and fast payback factor has tended many researchers around the globe working around the clock to increase the overall DSSC performance. Highest lab – scale with a value of 12.3% efficiency has become new record that been reported recently (Yella et al., 2011). However, DSSC is required to achieve efficiencies over 15%, before able to compete with other type solar cell technology (S. Kim et al., 2013). Thus, instability and low efficiency become major challenges before the DSSC technology is commercially available in the market.

There are several approach that been used widely to enhance overall output efficiency. In general, higher porosity film will increase its specific expose surface area. Altering the porosity of existing the TiO_2 film to increase the number of dye embed with this surface is one of commonly studied approach (Yu et al., 2011). This will introduce new expand area for contact between dye – absorbed surface and solar radiation. Thus, higher efficiency DSSC was observed with this type of approach (He, Zhu, Li, Zhou, & Wei, 2011; Jung, Kwak, Hwang, & Yi, 2012; Lee et al., 2009).

However, the highly porous arrangement of the existing TiO_2 layer may introduce an electrical short circuit between liquid redox electrolyte and the transparent conductive oxide (TCO) layer interface which causing limited efficiency conversion (Abdullah & Rusop, 2013; Jin et al., 2012; Zalas et al., 2011). This was supported by study of V. Dhas et al. shows the significant efficiency of prepared DSSC was observed drop from 5.6 ± 0.2% to 4.8 ± 0.2% as the TiO_2 become more porous (Dhas et al., 2011). Therefore, it is very important to improve the respective interfacial contact to enhance its efficiency and durability of the produced DSSC.

1.4 Motivation of the Study

To avoid leaking current problem in DSSC application, a compact anatase catalytic phase TiO_2 thin film as a passivation layer was suggested to be used between the TCO layer and existing TiO_2 layer to prevent any back transfer of electrons due to direct contact in any DSSCs (Karthikeyan et al., 2006; H.-J. Kim, Jeon, Kim, Lee, & Kwak, 2012). A study reported by Jin et. al., shows that by inserting this compact TiO_2 layer, the overall efficiency has increase up to 1.4% higher than existing without any extra layer at a value of 3.2% (Jin et al., 2012). Another similar study on the effect of TiO_2 compact layer thickness over DSSC performance was also reported by (Jeong & Kim, 2011). In this study, it has disclosed that as thickness increases from without TiO_2 passivation layer, 10 nm, 20 nm and 50 nm, the power conversion efficiency has increased from 3.8%, 4.18%, 4.20% and highest at 4.42%, respectively. Proper thickness value of the thin film layer is needed to increase the overall efficiency.

Few studies have been reported that high quality TiO_2 thin film has been fabricated using magnetron sputtering system. However, most of the study shows that pure TiO_2 ceramic has been used as sputter target (Jin et al., 2012). This type of target is commonly has a lower deposition rate during sputtering process, limited, fragile and very costly. To overcome this problem, a TiO_2 thin film will be prepared from pure Titanium (Ti) target as the starting material using reactive sputtering method. Several sputtering conditions will be performed to study and understand the atomic formation of TiO_2 molecules inside the chamber. Further study on the morphology, optical and electrical will help to determine good sputtering conditions to produce high quality anatase catalytic phase TiO_2 compact thin film to be used in DSSC.

1.5 Objectives of the Study

This research focused to improve the overall efficiency of existing DSSC by inserting passivation layer of anatase catalytic phase TiO_2 thin film deposited using magnetron sputtering technique. Following objectives to be studied during research work are as follows:-

(i) To evaluate the atomic particles formation of TiO_2 thin film that emitted from pure titanium target as starting material during reactive sputtering deposition.

(ii) To investigate the film morphology, optical and electrical of sputtered substrate using reactive sputtering deposition technique at various oxygen parameters.

1.6 Scope of the Study

This research is embarks the study objective based on following scopes:-

(i) To deposit compact and dense TiO_2 thin film using reactive sputtering technique with using pure Titanium target as starting material under various oxygen gas flows, i.e. from 0% to 20% ratio.

(ii) To characterization on atomic and ions lines of Ti, Ar, Ar^+, O and O^- intensity using optical emission spectroscopy (OES) and Langmuir probe analysis.

(iii) To characterization the morphology, optical and electrical properties using surface profiler, atomic force microscope (AFM), ultra violet – visible spectroscopy (UV – vis) and four point probe. Each result will be analyze and discussed at the end of the project.

1.7 Outline of the Thesis

This thesis will discuss on deposition and characterization of compact TiO_2 thin film fabrication using pure Titanium target as starting material in magnetron sputtering technique. The fabricated TiO_2 thin film will be later characterized to be used in DSSC application. The prepared TiO_2 thin film was aim to reduce the recombination factor between the liquid redox electrolyte and TCO layer. The efficiency improvement of DSSC will be discussed.

This thesis consists of 5 chapters in total. After the brief introduction and research motivation in Chapter 1, the related literature review will be discussed in detail in Chapter 2. Introduction of thin film and sputtering deposition method will be explained. The working properties of plasma during sputtering deposition will be enlightened with aid of relative pictures. The comparison between silicon type solar cell and DSSC will be discussed.

Chapter 3 is devoted to characterization of reactive plasma environment during the deposition of TiO_2 thin film in reactive sputtering system. This characterization involves plasma distribution measurement of strong atomic lines such as Ti, Ar, Ar^+, O and O^-, the plasma electron temperature, plasma density and ion density. Several equipments will be setup and used to measure the plasma environment without disturbing the plasma plume using inside the deposition chamber.

Chapter 4 deals characterisation on the morphology, optical and electrical properties of prepared TiO_2 thin film. Working procedure of related equipment such as surface profiler, AFM, uv – vis and four point probe will be explained. Resultant result will be analyzed and discussed in detail.

Chapter 5 is devoted on overall conclusion of the whole research study. Recommendation will be suggested at the on the study based on the conclusion obtained.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction to thin film fabrication

Thin film technology has become a sophisticated and rapidly growing technology used in various fields. Thin film can be defined as layers ranging from nanometers to several micrometers in thickness (Mattox, 1998). The need of thin film formation is to achieve a new desired properties which not easily attainable from the bulk material (substrate) alone. Surface modification through thin film fabrication can exhibit an alteration in atomic, electrical, mechanical, optical, thermal and magnetic properties through surface variation in material composition, doping, multilayer film fabrication and lithographic patterning (Smith, 1995). Fundamental knowledge in material science and surface structure is crucial to enhance the required properties depending on the applications need.

Several applications that manipulate thin film as base technology are used in making of sensors, batteries, optical instrument, solar cell, ceramics, microwave communication, military and others. Custom patterned with complex structure thin film is widely used as electrical conductor films, optical film for transmission and reflection, permeation barrier for moisture and gas, electronic insulation, magnetic film for recording and others. Such vast application are highly depends on various properties such as type of material, particle grain size, density, particles adhesion, porosity, film thickness, film crystality, conductivity, material composition stoichiometry, topography and morphology, hardness and magnetic (Mattox, 1998; Smith, 1995). It is essential to study and alter these parameter properties using suitable deposition techniques to suit as the application need.

2.2 Thin film deposition technique

Thin film deposition can be derived as an act of applying a layer (film) onto a substrate surface resulting new properties response emit from the existing bulk material (substrate). Advance fabrication techniques are designed to manipulate atomistic film deposition process to form preferable thin film layer on a substrate. An atomistic film deposition can be defined as process to deposit desire material film by atom-by-atom (Mattox, 1998). Such atom – by – atom fabrication method able to introduce a thin film with varying density value (high density – porous), single crystal to amorphous condition, a certain level of purity and custom thickness level. The deposition process should be controllable to obtain high quality homogenous film with excellent properties response.

To achieve high quality homogenous thin film, there are two methods of stable thin film deposition technique has been reported widely in active research papers, that is, the Physical Vapour Deposition (PVD) and the Chemical Vapour Deposition (CVD) technique. The general idea of PVD method is to evaporate a solid or liquid metal before condense on a substrate to form film, while the CVD method requires high temperature reduction with the help of suitable precursor to form material vapour (such as Ga to GaCl) before deposited the resultant thin film. Both PVD and CVD method are used widely to form high quality thin film. However, the PVD method shows some advantage over the CVD method in several aspects as follows:-

i. PVD method can be used to deposit on various type and shape of substrates. These criteria allow one to deposit a wide range of metal or composition on low melting point material such as thin and flexible thermoplastics. On the other hand, in CVD method, it involves a high deposition temperature process (may exceed 600°C), where this practice may intrude the existing custom fabricated structure on the substrate.
ii. Several CVD precursor (hydrides and carbonyls) used in the deposition process are often hazardous or toxic. Byproduct of this type of precursor is not environmentally friendly compared to PVD method. Example often used precursors are Arsine and Cyanide.

iii. CVD method leads to numerous parameters to be precisely controlled and monitored during fabrication process. This makes the CVD system handling, difficult compared with PVD method.

In this section, PVD method will be focused and discussed deeply as follows due to its significant advantage and the facility is locally available over CVD method.

2.3 Introduction to Physical Vapour Deposition (PVD)

The first reported sputtering phenomena (part of PVD process) was by W.R. Grove in 1852 while studying a glow discharge device. However, the term "PVD" were only introduced by C.F. Powell, J.H. Oxley and J.M. Blocher Jr. in their book "Vapor deposition" in 1966 even though PVD process has been reported earlier. Since the first innovation, PVD has undergone various evolutions till becomes one of fundamental and stable technique to fabricate thin film. The general idea of this fabrication technique is to have material that vaporized from solid or liquid source in form of atoms or molecules, transported in the form of a vapour through a vacuum or low pressure gaseous (or plasma) environment to the substrate where it condenses before settle in thin film form (Mattox, 1998). This technique significantly involved atomistic deposition processes which coats entire exposed substrates in reachable range. The main category of PVD processing is vacuum evaporation, sputter deposition and ion platting.

All PVD processes category can generally divided into 4 major steps, that is, 1) source, 2) transport, 3) deposition and 4) thin characterization. In PVD process, the film – forming starting material source can be in various phase form such as solid, liquid, vapour or gas. Solid phase will be the priority phase source used with PVD method due to its stability and ease of handing. Material in form of solid need to be vapourized before transport them towards targeted substrate. This evaporation process can take place using several technique such heating, energetic beam of electrons, photons (laser ablation) or positive ions (sputtering). Study on the vapour material supply rate is essential to determine the deposition rate of the fabrication.

During the vapour transportation process from source to substrate, aspect such as transportation medium is crucial to determine the uniformity of arrival rate on the substrate surface area. High vacuum environment creates larger mean free path that allows particles arrives uniform on substrate in straight line. Mean free path can be derived as the mean distance traveled by a single particle in a gas environment before encounter a collision with another molecule (Smith, 1995). Low vacuum environment will increase the collision frequency between energetic particles and gas molecules causing to lose some portion of energy and become thermalized due to ambient energy of the molecule. It is crucial to preserve high vacuum environment to obtain good uniformity of arrival rate during the deposition process take place. Further explanation on the vacuum environment will be discussed in section 2.4.4.

The third part of deposition process will be the deposition on substrate surface. In this step, the overall deposition process is determined by two main factors which is surface condition and reactivity of depositing material. Surface condition is referring to the morphology, level of surface oxidation (contamination) and degree of chemical bonding with arrival particles. These substrate conditions influence the overall film topography such as roughness at the end of deposition process. The reactivity factor during the fabrication process can be referred to the "sticking coefficient" of the depositing particle on the substrate surface. Nucleation process begins when arriving particles starts to aggregate with surface initial particles also known as seeding particles to form island of atoms. Higher number of new particle adhesion with the seeding particles will grow film with uniform thickness to embark new structure, film morphology and crystallography of this new thin film formed. The deposited film crystallography may in the range from amorphous to polycrystalline to single – crystal (Smith, 1995). Several in – situ monitoring technique can be applied during this stage to control and understand the film growing process. This in – situ feedback will help researchers to understand manipulate the process to form better film properties for required applications.

The final part of the deposition process will emphasis on the ex-situ analysis on the surface of formed film. There are various techniques can be used to study the direct properties such as roughness, thickness, hardness, index of film reflection,

particle size grain and others. Example of equipments used to study those properties is surface profiler, Atomic Force Microscope (AFM), Scanning Electron Microscope (SEM) and others. Further deep analyses can also be done to understand the structure and composite of the resultant film using equipment such as X-ray Photoelectron Spectroscopy (XPS), Auger Electron Spectroscopy (AES), Rutherford Backscattering Spectroscopy (RBS), Transmission Electron Microscope (TEM), X-ray Diffraction (XRD), Four Hand Probes and others. All these surface analysis approaches can be used to study and enhance the know-how and properties knowledge of fabricated film using PVD technique. The sputtering deposition technique will be further discussed as follows.

2.4 RF Magnetron Sputtering System

Magnetron sputtering deposition technique is one of advance and sophisticated PVD technique used commonly to deposit high quality and uniform solid thin film. In this process, vaporized particles originate from solid target source will be deposited on substrate without any thermal process (evaporation) in use. The first sputtering deposition was reported by Wright in 1877 and further studied by Edison who patterned silver on wax photograph cylinder deposition in year 1904. Since then, sputtering technique have undergoes intensive study to form high quality thin film with significant properties depending on application needs.

Sputtering can be define as process that involves bombardment of high energetic plasma ions on the surface of sputtering metal, which cause to dislodged a physical target atom to vaporised and then condense into a thin film of the target material (Mahan, 2000). It uses low – pressure high energetic ionized environment (positive and negative ions) to deposit atom or molecules particles on any type of substrate at atomistic precise level. The advantage of sputtering process includes simple apparatus, high deposition rate, low substrate temperature, good surface flatness, transparency and dense layer formation (Ki Hyun et al., 1997). These significant advantages has led the magnetron sputtering techniques used in various important industrial coating which includes hard coating, wear – resistant coatings, low friction coatings, corrosion – resistance coatings, decorative coatings and coating

with specific application properties (Kelly & Arnell, 2000). Resultant coating has been used radically in many vital applications such as in optical coating, piezoelectric material, solar cell, diffusion barrier layers in electronics applications and others.

Various types of pure metal, ceramic oxides and composition thin film can be growth with high rate of repeatability and reliability using this sputtering technique. Thin film Copper (Cu), Zinc (Zn), Gold (Au), Titanium dioxide (TiO_2), Silicon Dioxide (SiO_2), Aluminium Oxide (Al_2O_3), Silicon Carbide (SiC) and Titanium Aluminium Nitrate (TiAlN) are few examples that can be produced using this technique. Several parameters can be used to control thin film properties such as type of target material, different type of reactive gas, discharge power rating, amount of working gas pressure, the gases ratio, target-substrate distance and substrate temperature (Chapman, 1980). By controlling these type of dependence parameters, resultant film properties can be alter to suit any needed application (Senthilkumar et al., 2010).

As mention previously, the basic principle of magnetron sputtering configuration is to form denser plasma at near surface target (cathode) at low pressure so that ions can be accelerated towards cathode without losing of energy due to the physical and charge – exchange collisions (Mattox, 1998). Regarding to this matter, magnetron sputtering system needs few major part connected together to support deposition process of uniform film. There are deposition chamber, sputtering source, sputter target, rotatable substrate holder, substrate heater, gas supply, water cooling system, vacuum system, vacuum gauge, power discharge control and pressure valve controller. Each and every part is fixed together to from working magnetron sputtering machine as shown in Figure 2.1 and Figure 2.2. Selected target material (e.g. pure Titanium target) will be attached on the sputtering source holder, opposite with the substrate holder inside the chamber. Another end of the sputtering source will be connected with radio frequency (RF) on left side and direct current (DC) on right side with automatic matching box which is located on the top of the chamber. Both sputter source need constant flow of chilled water to avoid any overheated on the target surface. Samples that need to be deposited will be placed on the substrate holder and taped with Teflon tape to reduce any moment before or

during the deposition process held. Heating element that located at the bottom of the substrate holder is an optional device to enhance chemical bonding between condensed particles during fabrication process.

Figure 2.1: Advance Magnetron Sputtering system from Syntex Co., located in Microelectonic and Nanotechnology – Shamsuddin Research Centre (MiNT – SRC).

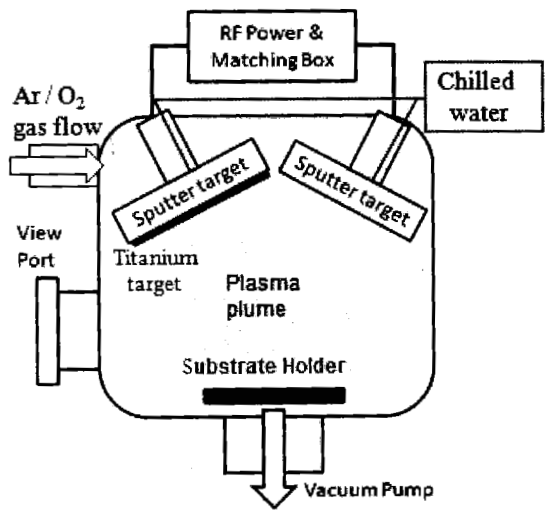

Figure 2.2 : The cross section of dual – target magnetron sputtering system.

Study shows that sputtering process need a good background vacuum environment before any deposition process starts. Such environment will reduce particle collision due to longer free mean path phenomena and may avoid any stoichometry change due to present of unwanted gas such as nitrogen, hydrogen or oxygen. Regarding this requirement, the deposition chamber usually will be supported with adequate vacuum pump such as rotary pump, turbo molecular pump and ion trapping pump. Constant amount of ambient gas such as Argon gas will later backfilled into the chamber and controlled using pressure valve controller as shown in Figure 2.2. At this particular point, the pressure reading is then referred as working pressure (WP).

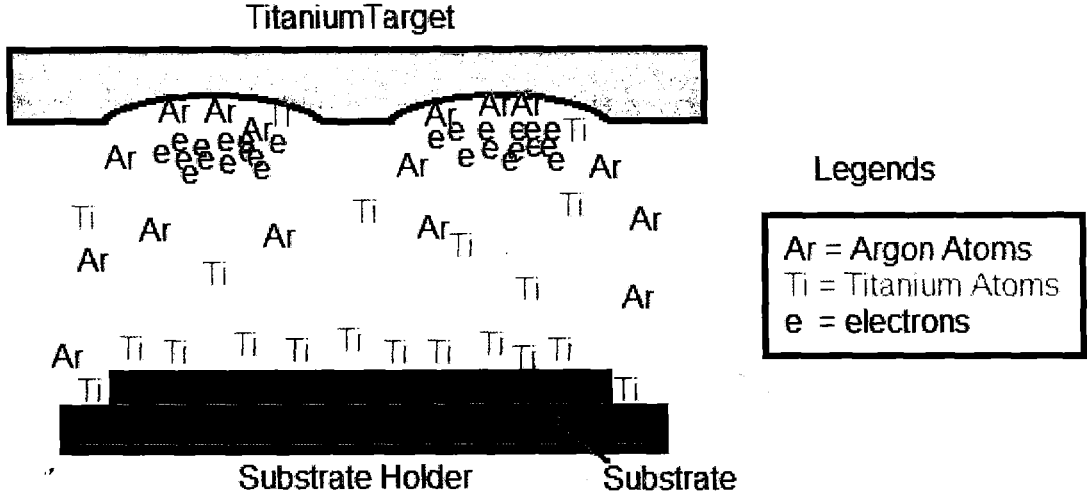

Figure 2.3 : The concept of plasma activity inside the deposition chamber.

Sufficient power supply is needed before any plasma sputtering environment created in the middle of the chamber, originated from sputter source (cathode). Positive ions from the ambient gas, i.e. Ar^+ are accelerated towards cathode with high speed before bombarding the target surface and physically releasing respective atom (Ti atoms) into the environment as shown in Figure 2.3. There are large probabilities these atom particles will condense on substrate forming a strongly attached monolayer of thin film. Reactive gas such as oxygen and nitrogen may be

inserted into the chamber at controlled volume to activate reactive sputtering deposition. Any plasma activity inside the chamber can be visualized through quartz glass view port as illustrated in left side of the Figure 2.2. Study on the plasma formed inside the magnetron sputtering is crucial to provide better understanding on atomic activities during the growth of thin film. Further description of each part of the sputtering is explained in the next subsection.

2.4.1 Deposition chamber with coolant flow system

Sputtering chamber is usually made of high quality stainless steel that generally shaped in cylindrical shape. It contains few openings for various application and measurement need such as vacuum pump, sputter source, pressure sensor, gas inlet, temperature sensor, view port, opening window and others. In such condition, it is very important to have well sealed metal steel deposition chamber at all places especially at critical join area. Introduction of cracks on any part of the chamber will cause a gas leak where stable plasma environment may not be achieved. Chamber check up practice using helium detector may discover any gas leak out of the system. Also, frequent usage of sputtering system may introduce a thick dark coating around the chamber's wall that interferes with ability to achieve high vacuum environment in the system. This unwanted coating can be slowly removed later using sand blasting process.

In addition, high quality quartz glass is usually mounted on view port for plasma visualization during fabrication process. The quartz made glass is commonly used to allow wider wavelength spectrum to penetrate through the glass for spectra acquisition on the plasma produced. Laser aided optical emission activities observation is made possible due to this advantage especially at low wavelength regions (lower than λ = 300 nm). Rotatable view shutter is placed on the view port and used to shield the respective glass from being coated from inside during the fabrication process.

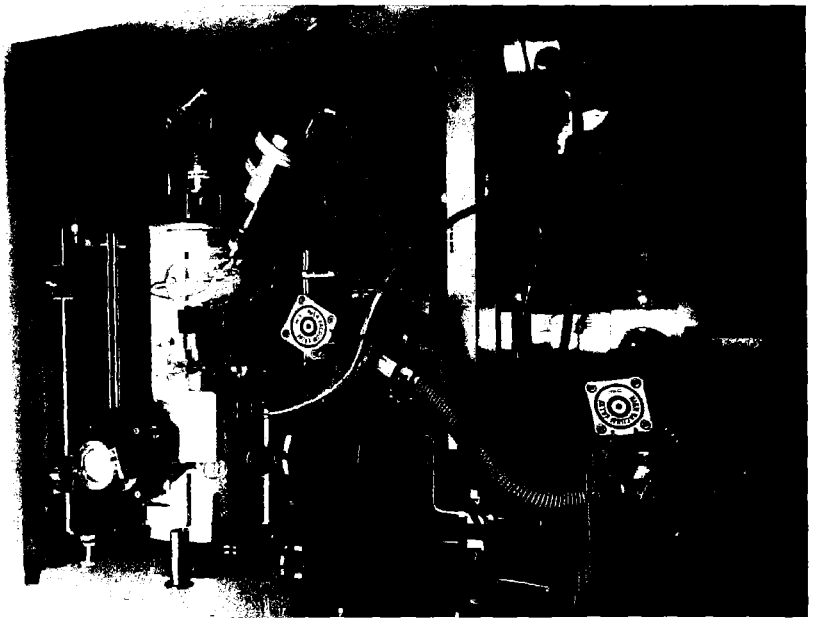

Figure 2.4 : The magnetron sputtering deposition chamber with 6 view port & water coolant flow system.

Vigorous energy collision activity on the target surface will cause power to loss and dissipate in form of heat. Significant amount of heat are commonly sensed on wall chamber and sputtering source surface. To avoid any future damage due to this intensive heat grow inside the chamber, a reliable coolant system were design to always make contact around the deposition chamber and sputter target to disperse heat out efficiently. Most common type of coolant used is chilled water (not cryogen type) which been kept constant at slightly lower than normal room temperature, i.e. 19.7°C. Water flow is adjusted to flow constantly about 2 liters per minute (L/min). Higher flow rate will cause inefficient heat absorption by coolant. Any failure of controlling dissipated heat will cause sputter target to swollen before introduce fracture or break apart. Further discussion regarding the sputter target matter will be discussed in section 2.4.3.

2.4.2 Magnetron sputtering source

In the conventional sputtering process, electrons that ejected tend to accelerate away from the cathode surface causing unsustainable plasma discharge occur inside the deposition chamber. Irregular plasma discharge will cause an unstable and unreliable

deposition rate. To overcome such phenomena, strong magnetic field is been introduced to trap electron clouds between the closed flux path and make to circulate on the closed path on the cathode surface. This closed flux path pattern is highly depends on ways of magnetic arrangement at the behind of the target surface. Therefore, higher number of ionized radicals, Ar^+ will bombard rapidly on the target source at very specific region (depends on the magnetic arrangement as mention earlier) causing to create a denser plasma environment inside low pressure chamber. This will allow higher overall sputtering deposition rate at lower potential rating on target than with conventional sputtering process. This magnetic assist sputtering is known as magnetron sputtering system.

There are 3 types of magnetic assist sputtering source used widely, i.e. planar, cylindrical and circular. The most commonly used in the industry is the planar type, where strong permanent magnetic pole pieces are arranged in form of complete circle on flat conductive surface (usually copper). Resultant of this arrangement produce either closed circle or elongated circle magnetic flux on target surface. Figure 2.5 shows the typical arrangement of balanced magnets with closed circle path on sputter source. Most positive ions bombardment will occur in the very specific region between north-south fluxes of magnets. Such arrangement will cause a close ring of sputter – erosion (utilization) path to appear on the target surface after using for a long occasion.

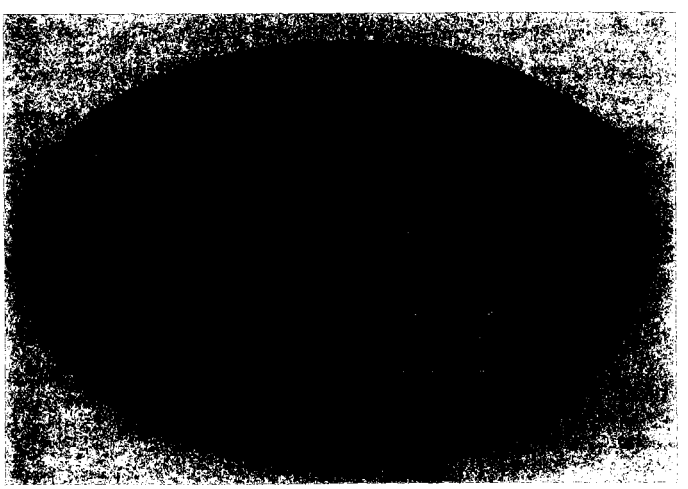

Figure 2.5 : Used 3 inches plannar sputter source with close ring of sputter – erosion appear after long sputtering usage.

In sputtering deposition, there are two major types of discharge power source configuration. There are direct current (DC) and radio frequency (RF) discharge type. Most of the time, DC discharge is used to fabricate pure conductive material only such as Aluminium (Al), Platinum (Pt), Copper (Cu), Gold (Au), Silver (Ag) and others. DC discharge using non conductive (insulating) target will cause a built up of surface charge that prevents further ion bombardment on the surface target. Lower ion bombardment activity will slow down the deposition rate if this fabrication conditions is constantly continued. Any reactive (oxides and nitrites) deposition using pure conductive material in DC discharge will cause similar surface charge built up due to the target poisoning phenomena and may introduce arcing or spikes on the surface.

Contrast with DC discharge, the RF type source can be used to fabricate both of conductive and non-conductive materials. RF type discharge which capacitively coupled inside an automatic matching box produces alternating potential with large peak to peak voltage. During first part of half – cycle, ions are accelerated to the target surface with enough energy to remove respective atom while on alternate half – cycle, electrons will reach the surface to prevent any built up charges (Mattox, 1998). This conventional sputtering frequency of RF discharge is set to 13.56 MHz in value. RF discharge arrangement can be used to fabricate ceramic and insulating materials even though it deposit at low deposition rate. Any significant high discharge power on insulating material may resultant in a fracture on sputter target surface occurs due to its nature being fragile material.

The DC type fabrication can be done at higher working pressure than normal (starting from 30 mTorr up to several 100 mTorr) which may result higher deposition rate compared to RF type discharge. All discharge power rating on sputter target are been controlled using computerized power controller attached in the system. However, user must maintain power distribution on sputter target below than 10 Watt/cm^2 to avoid any target damage due to overheating or uncontrollable release of atomic particle size. A steady power ramping up and down with average of 10 Watt/minute will help to increase the lifespan of sputter target. Further discussion on sputter target is discussed in section 2.4.3.

2.4.3 Sputter Target

Depending on the application need, sputter target can be selected from various types of metal element or ceramic composite, ratio composition, purity, thickness, size and shape. Various sputtering target configurations are available in market that includes planar target, hollow cylindrical target and conical target. The most common purchased will be the planar type. Usually, planar sputtering target that made of basic element materials such as Al, Ti, Cu, Pt, Au and others are commercially available all the time. However, custom made target from rare material or specific composition will be prepared as requested by the user. All target element are been differentiate based on purity scale in percentage (%) value. Target with larger significant figure (as nearer to 100%) will generally provide higher purity resultant thin film fabrication. Generally, the price of sputter target goes up rapidly with purity scale, material composition and material rareness. However, drawback of any sputter target used in magnetron sputtering system is that only used about 30 – 50% of its weights before scrapped due to specific area ions bombardment as discussed early in section 2.4.2.

Another factor to be considered during target purchase is the amount of porosity that present on sputter target. Any target with below than 96 % density will resultant with series of pores interconnected each other, ending as a porous material. This situation will contribute some virtual leaks and acts as a contamination sources inside a vacuum chamber. Porous targets are able to absorb and hold water content from atmosphere environment and introduce some processing difficulties during fabrication process such as lengthen vacuum down time up to more than twice longer and alter plasma resultant properties (Smith, 1995). Any contamination on surface material arrangement may vary the overall deposition rate and plasma density characteristics due to dissimilar in secondary electron emission at the surface (Mattox, 1998). Proper thermal baking outside chamber will outgass any trapped unwanted moist or gases between the porous gap on sputter target.

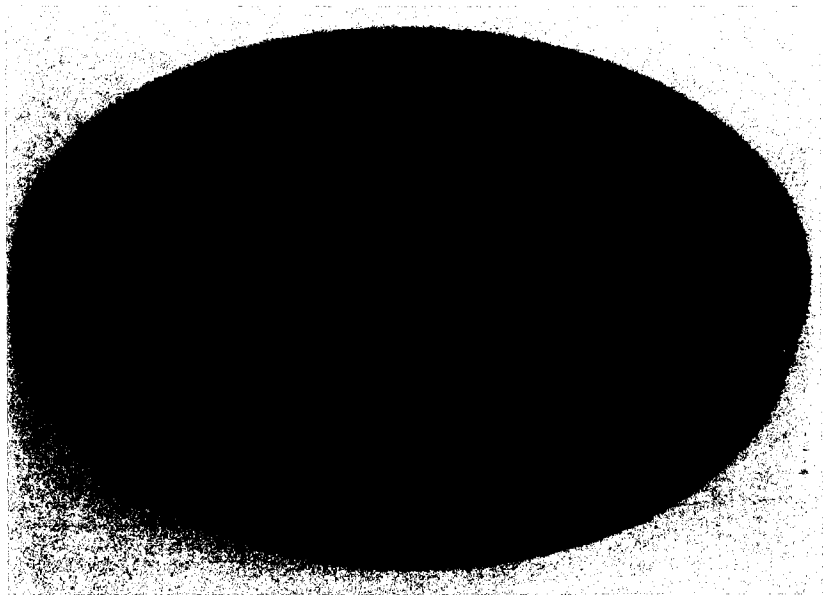

Figure 2.6 : Copper backing plat target for good heat disperse.

Typical for non conductor materials such as oxides composite, they are bonded with Cu backing plate for heat and current dissipates purpose. During fabrication process high heat were produce due to vigorous ion bombardment on sputter target inside the chamber. Copper backing plate provides a good thermal contact for heat disperse between coolant flows and sputter target. If the target material is brittle, any failure in cooling system will cause target to expand and introduce swollen or fractures. All sputter targets must be handed with high caution which includes avoidant of bare hand touching and place in dry cabinet. In addition, before any fabrication process takes place, sufficient amount of pre – sputtering practice inside chamber is needed to eliminate any formation of contamination layer on the target surface. Examples of fractured sputter targets are shown in Figure 2.7.

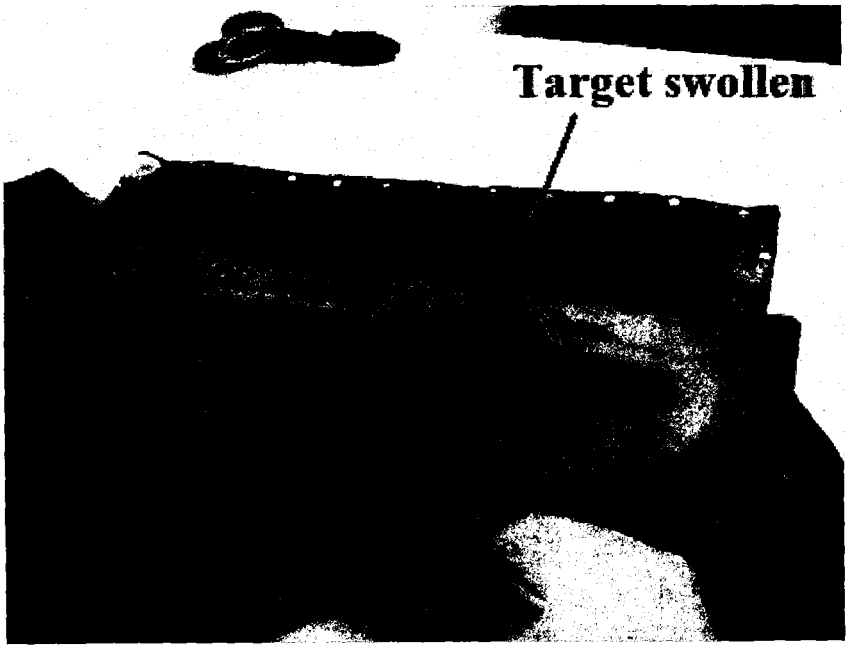

Figure 2.7: Figure of swollen large Titanium target due to water cooling failure. Picture is courtesy from Faculty of Mechanical Manufacturing, UTeM.

2.4.4 Vacuum system

As per mention before, vacuum system plays important role in sputtering process. Vacuum can be define as volume that contains fewer gaseous molecules than the ambient environment when both contains the same gaseous species and are at the same temperature (Mattox, 1998). Vacuum environment is crucial to introduce a longer mean free path for particles arrive uniformly on substrate before collide with other gas species inside the chamber. Mean free path can be defined as average distance traveled by moving particles such as atom and gas molecules between successive impacts or collisions which modify its direction or energy or other particles properties (Mattox, 1998). High pressure environment inside deposition chamber will increase the probability of collision between energetic particles and gas molecules causing to lose some portion of energy and become thermalized due to ambient energy of the molecule. Maintaining a good vacuum environment is crucial to minimize these collisions factor and provide uniform arrival rate during the fabrication process.

REFERENCES

Abdullah, M. H., Ismail, L. N., Mamat, M. H., Musa, M. Z., & Rusop, M. (2013). Novel encapsulated ITO/arc-ZnO:TiO_2 antireflective passivating layer for TCO conducting substrate prepared by simultaneous radio frequency-magnetron sputtering. *Microelectronic Engineering, 108*(0), 138-144.

Abdullah, M. H., & Rusop, M. (2013). RF sputtered tri-functional antireflective TiO2 (arc-TiO2) compact layer for performance enhancement in dye-sensitised solar cell. *Ceramics International.*

Ahn, K.-S., Kang, M.-S., Lee, J.-W., & Kang, Y. S. (2007). Effects of a surfactant-templated nanoporous TiO_2 interlayer on dye-sensitized solar cells. *Journal Of Applied Physics, 101*, 84312.

Belkind, A., Zhu, W., Lopez, J., & Becker, K. (2006). Time-resolved optical emission spectroscopy during pulsed dc magnetron sputter deposition of Ti and TiO_2 thin films. *Plasma Sources Science and Technology, 15*(2), S17.

Chapman, B. N. (1980). *Glow discharge processes: sputtering and plasma etching*: Wiley.

Chen, G. S., Lee, C. C., Niu, H., Huang, W., Jann, R., & Schutte, T. (2008). Sputter deposition of titanium monoxide and dioxide thin films with controlled properties using optical emission spectroscopy. *Thin Solid Films, 516*(23), 8473-8478.

Dang, B. H. Q., MacElroy, D., & Dowling, D. P. (2013). Achieving enhanced DSSC performance by microwave plasma incorporation of carbon into TiO_2 photoelectrodes. *Applied Surface Science, 275*(0), 289-294.

Dhas, V., Muduli, S., Agarkar, S., Rana, A., Hannoyer, B., Banerjee, R., et al. (2011). Enhanced DSSC performance with high surface area thin anatase TiO_2 nanoleaves. *Solar Energy, 85*(6), 1213-1219.

Di Paola, A., Cufalo, G., Addamo, M., Bellardita, M., Campostrini, R., Ischia, M., et al. (2008). Photocatalytic activity of nanocrystalline TiO_2 (brookite, rutile and brookite-based) powders prepared by thermohydrolysis of $TiCl_4$ in aqueous chloride solutions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 317*, 366-376.

Dreesen, L., Colomer, J.-F. o., Limage, H., GiguÃre, A., & Lucas, S. p. (2009). Synthesis of titanium dioxide nanoparticles by reactive DC magnetron sputtering. *Thin Solid Films, 518*(1), 112-115.

Ferrere, S., & Gregg, B. A. (1998). Photosensitization of TiO2 by [Fe II(2,2-bipyridine-4,4-dicarboxylic acid)$_2$(CN)$_2$] Band Selective Electron Injection from Ultra-Short-Lived Excited States. *Journal of the American Chemical Society, 120*(4), 843-844.

Flores, M., Huerta, L., Esçamilla, R., Andrade, E., & Muhl, S. (2007). Effect of substrate bias voltage on corrosion of TiN/Ti multilayers deposited by magnetron sputtering. *Applied Surface Science, 253*(17), 7192-7196.

Gaillard, M., Britun, N., Yong, M. K., & Jeon, G. H. (2007). Titanium density analysed by optical absorption and emission spectroscopy in a dc magnetron discharge. *Journal of Physics D: Applied Physics, 40*(3), 809.

GrÃtzel, M. (2003). Dye-sensitized solar cells. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews, 4*(2), 145-153.

GrÃtzel, M. (2005). Solar Energy Conversion by Dye-Sensitized Photovoltaic Cells. *Inorganic Chemistry, 44*(20), 6841-6851.

Gu, G.-r., He, Z., Tao, Y.-c., Li, Y.-a., Li, J.-j., Yin, H., et al. (2003). Conductivity of nanometer TiO2 thin films by magnetron sputtering. *Vacuum, 70*(1), 17-20.

Hayashi, Y., Hirao, S., Zhang, Y., Gans, T., Connell, D. O., PetroviÄ, Z. L., et al. (2009). Argon metastable state densities in inductively coupled plasma in mixtures of Ar and O_2. *Journal of Physics D: Applied Physics, 42*(14), 145206.

He, Z., Zhu, Z., Li, J., Zhou, J., & Wei, N. (2011). Characterization and activity of mesoporous titanium dioxide beads with high surface areas and controllable pore sizes. *Journal of Hazardous Materials, 190*(13), 133-139.

Hurum, D. C., Agrios, A. G., Gray, K. A., Rajh, T., & Thurnauer, M. C. (2003). Explaining the Enhanced Photocatalytic Activity of Degussa P25 Mixed-Phase TiO_2 Using EPR. *The Journal of Physical Chemistry B, 107*(19), 4545-4549.

Ito, S., Kitamura, T., Wada, Y., & Yanagida, S. (2003). Facile fabrication of mesoporous TiO_2 electrodes for dye solar cells: chemical modification and repetitive coating. *Solar Energy Materials and Solar Cells, 76*(1), 3-13.

Jeong, J.-A., & Kim, H.-K. (2011). Thickness effect of RF sputtered TiO_2 passivating layer on the performance of dye-sensitized solar cells. *Solar Energy Materials and Solar Cells, 95*(1), 344-348.