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EFFECT OF DEPOSITION TEMPERATURE AND TYPE OF SUBSTRATES ON STRUCTURAL, SURFACE MORPHOLOGY AND OPTICAL PROPERTIES OF RF MAGNETRON SPUTTERED CCTO THIN FILM

By

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled "**Effect of Deposition Temperature and Type of Substrates on Structural, Surface Morphology and Optical Properties of RF Magnetron Sputtered CCTO Thin Film**". I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or University.

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Date: 1 June 2017

Witnessed by

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TABLE OF CONTENTS

Contents **Page**

LIST OF TABLES

Page

LIST OF FIGURES

Page

LIST OF ABBREVIATIONS

AC	Alternating Current
AFM	Atomic Force Microscopy
AZO	Aluminium Doped Zinc Oxide
BSE	Back-Scattered Electron
CCTO	Calcium Copper Titanate
CVD	Chemical Vapour Deposition
DC	Direct Current
EDX	Energy Dispersive X-Ray Spectroscopy
FESEM	Field Emission Scanning Electron Microscopy
FTO	Fluorine Doped Tin Oxide
FWHM	Full Width at the Half Maximum
HOMO	Highest Occupied Molecular Orbital
ICDD	International Centre for Diffraction Data
ITO	Indium Doped Tin Oxide
JCPDS	Joint Committee on Powder Diffraction Standards
LUMO	Lowest Unoccupied Molecular Orbital
MOCVD	Metal-Organic Chemical Vapour Deposition
PLD	Pulsed Laser Deposition
PVD	Physical Vapour Deposition
RF	Radio Frequency
RMS	Root Mean Square
sccm	Standard Cubic Centimeter Per Minute
SEI	Secondary Electron Imaging
UV-vis	Ultraviolet-Visible

XRD	X-Ray Diffraction
YIG	Yttrium Iron Garnet

LIST OF SYMBOLS

%	Percentage
°	Degree
°C	Degree Celcius
Å	Angstrom
A_a	Area of Amorphous
A_c	Area of Crystalline
c	Velocity of Light
cm	Centimeter
Eg	Optical Energy Band Gap
eV	Electron Volt
h	Hour
hν	Photon Energy
κ	Dielectric Constant
K	Kelvin
kHz	Kilo Hertz
mbar	Millibar
MHz	Mega Hertz
min	Minute/s
mm	Millimeter
N	Newton
N_d	Number of Dopant
nm	Nanometer
Pa	Pascal
ppm	Part Per Million

Ra	Surface Roughness
tan δ	Tangent Loss
W	Watt
Z	Atomic Number
β	Full Width at the Half Maximum
δ	Dislocation Density
ε	Dielectric Permittivity
θ	Theta
λ	Lambda
μm	Micrometer
με	Microstrain
χ_c	Degree of Crystallinity

KESAN SUHU PEMENDAPAN DAN JENIS SUBTRAT KEPADA CIRI-CIRI STRUKTUR, MORFOLOGI PERMUKAAN DAN OPTIK BAGI FILEM NIPIS CCTO SPUTER MENGGUNAKAN MAGNETRON FREKUENSI RADIO

ABSTRAK

Filem nipis kalsium kuprum titanium oksida (CCTO) mempunyai ketelusan dielektrik yang tinggi, kehilangan tangen yang rendah dan fasa stabil di suhu tinggi mencecah 300 °C adalah sangat penting dalam sesetengah aplikasi mikroeletronik. Ciri-ciri eletrik dan optik bergantung kepada struktur dan morfologi permukaan filem nipis CCTO. Tujuan projek ini adalah menyelidik kesan-kesan suhu pememdapan dan substrat yang berbeza (ITO, FTO dan kaca) terhadap struktur, morfologi permukaan dan ciri-ciri optik filem nipis CCTO. Pertama sekali, filem nipis CCTO telah dipendapkan ke atas substrat yang berbeza (ITO, FTO dan kaca) dengan suhu pememdapan 100, 150, 200 dan 250 °C. Cara pemendapan digunakan ialah sputter menggunakan magnetron frekuensi radio dalam atmosfera Argon. Struktur, morfologi permukaan dan ciri-ciri optik bagi filem nipis CCTO telah dikaji dengan menggunakan kaedah belaun sinar-X (XRD), mikroskopi daya atom (AFM), mikroskopi pengimbasan elektron pancaran medan (FESEM), spektroskopi serakan tenaga sinar-X (EDX) dan ultraunggu-nampak (UV-vis). Analisis XRD menunjukkan filem nipis CCTO pada substrat ITO dan FTO mempunyai puncak intensiti yang paling tinggi di (022), manakala hampir semua filem nipis CCTO pada substrat kaca menunjukkan amorfus struktur. Selain itu, penghabluran filem nipis CCTO pada substrat ITO dan FTO mennigkat apabila suhu pememdapan

meningkat. FESEM hanya boleh mendedahkan saiz butiran bagi filem nipis CCTO pada substrat ITO dan saiz butiran akan meningkat apabila suhu pemendapn meningkat. Analisis AFM menunjukkan permukaan substrat FTO yang kosong mempunyai 6 kali ganda kasar berbanding dengan substrat ITO dan kaca, oleh itu, filem nipis CCTO pada substrat FTO mempunyai permukaan yang kasar dan saiz liang yang besar. Tambahan pula, peningkatan suhu pememdapan akan menyebabkan peningkatan dalam kekasaran permukaan dan saiz liang. Kaedah Tauc plot digunakan untuk menjangka jurang band tenaga optik filem nipis CCTO. Jurang band tenaga optik filem nipis CCTO dijangka menurun dari 3.50 eV ke 3.14 eV (ITO), 3.52 eV ke 3.10eV (FTO) dan 3.58 eV ke 3.10 eV (kaca) dengan peningkatan suhu pemendapan dari 100 °C ke 250 °C. Konklusinya, dengan mengawalkan suhu pemendapan dan jenis subtrat, ciri-ciri filem nipis CCTO yang bagus boleh dihasilkan.

EFFECT OF DEPOSITION TEMPERATURE AND TYPE OF SUBSTRATES ON STRUCTURAL, SURFACE MORPHOLOGY AND OPTICAL PROPERTIES OF RF MAGNETRON SPUTTERED CCTO THIN FILM

ABSTRACT

Calcium copper titanate (CCTO) thin film with high dielectric permittivity (ε), low tangent loss (tan δ) and have high temperature phase stability up to 300 °C is very importance for several advanced microelectronic applications. The electrical and optical properties are depended on the structural and surface morphology of CCTO thin film. This project aims to study effect of deposition temperature and type of substrates (ITO, FTO and glass) on the structural, surface morphology and optical properties of sputtered CCTO thin film. Firstly, CCTO thin films were deposited on different type of substrates (ITO, FTO and glass) at deposition temperatures of 100, 150, 200 and 250 °C by RF magnetron sputtering in Argon atmosphere. The structural, surface morphology and optical properties of the deposited CCTO thin film have been studied by X-ray diffraction (XRD), atomic force microscopy (AFM), field emission scanning electron microscopy (FESEM), energy-dispersive X-ray spectroscopy (EDX) and ultraviolet-visible (UV-vis) spectrophotometer. XRD analysis showed CCTO thin films on ITO and FTO substrates have a highest intensity peak at (022) while CCTO thin film on glass substrates showed almost amorphous in structure. Besides, crystallinity of CCTO thin film on ITO and FTO increased with increase of deposition temperature. FESEM only able to reveal the crystallite size of CCTO thin film on ITO substrates and the crystallite size is increased with increase of deposition temperature. AFM analysis

showed the blank FTO substrates with 6 times rougher than blank ITO and glass substrates caused the CCTO thin film on it have significant higher in surface roughness and pore size. This is due to CCTO thin film are highly dependent on the surface feature of substrate. Increase of deposition temperature have increased the surface roughness (Ra) and pore size respectively. In addition, Tauc plot method was used to estimate the optical energy band gap of the deposited CCTO thin film. Optical energy band gap of the CCTO were decreased from 3.50 eV to 3.14 eV (ITO), 3.52 eV to 3.10 eV (FTO) and 3.58 eV to 3.10 eV (glass) as deposition temperature increased from 100 °C to 250 °C. Therefore, favourable CCTO thin film properties can be possibly obtained for particular application by controlling deposition temperature and using different type of substrates.

CHAPTER 1

INTRODUCTION

1.1 Background

In recent year, scientists have turned their efforts towards other materials to fulfill the needs of various niche applications. High dielectric permittivity (ε) or high-κ materials are one of the importance materials to improve and develop their excellent performance as electronic devices. Generally, the materials with ε higher than 1000 can be known as high ε materials (Zhang et al., 2016a). The common high ε materials are ferroelectric materials such as $(Ba,Sr)TiO_3$ and $Pb(Zr,Ti)O_3$, presenting values between 1000 and 1500 (Kim et al., 2004). High ε property is very importance in the microelectronic era, it allows smaller capacitive components, thus promote the decrease in the size of electronic devices and increase their performance as well as give advantage for space occupied. However, most of the high ε materials have ferroelectric property, therefore the ε of these materials are temperature-dependent accompanying lattice phase transition, which is not suitable and desirable for some higher operating temperature application devices (Subramanian et al., 2000).

To address this problem, high ε materials with high temperature stability was investigated. One of the materials fulfill these criteria is $CaCu_3Ti_4O_{12}$ (CCTO). CCTO is a novel metal oxide compound that have high ε, low tan δ and phase stability up to 300 °C (Löhnert et al., 2015). With these desired properties, CCTO has been paid much more attention nowadays. As the result, high ε materials (CCTO) are widely used in the technological application such as capacitors, antennas, microwave devices and sensors (Ahmadipour et al., 2016b). This showed that CCTO serves a precious value of research.

However, in microelectronics applications, CCTO thin films are much more interesting than CCTO ceramics or pellet due to thin film form CCTO have better properties than pellet form CCTO such as thickness uniformity and porosity distribution. Hence, high ε CCTO deserved to be reliable demonstrated and studied specifically in thin films. Started from year 2011, CCTO thin film studied become familiar (Yang et al., 2014; Lin et al., 2015). Start from year 2016, there is significant development of research on CCTO thin film with about 17 published papers. The shifted of studied of CCTO ceramic or pellet to CCTO thin film lead to attract attention of researches to develop the techniques used to prepare CCTO thin film.

In current state, pulsed laser deposition (PLD) (Fang & Shen, 2003; Sabóia et al., 2011), metal organic chemical vapour deposition (MOCVD) (Nigro et al., 2007b), Sol Gel (Jin et al., 2007) and radio frequency (RF) magnetron sputtering (Prakash et al., 2008) methods has been used. Within these four methods, RF magnetron sputtering is the most widely used method and also have advantages of film uniformity, good adhesion, and high packing density (Swann, 1988; Sankaran, 2016). Even though RF magnetron sputtering method promotes many advantages to thin film deposition but there is limited researchers used this technique to prepare CCTO thin film. Therefore, effects of different parameters of RF magnetron sputtering deposition technique on CCTO film must be explored.

RF magnetron sputtering was used in this project to observe it various advantages over the traditional RF sputtering. The advantage of RF magnetron sputtering technology is it uses magnetic fields to keep the plasma in front of the target, intensifying the bombardment of ions. A highly dense plasma is the result of this physical vapour deposition (PVD) coating technology. Besides, since the plasma was keep in front of target, it did not bombard on the chamber's wall, therefore contamination on CCTO thin film can be minimized. Since substrate and CCTO is a non-conductive material, therefore alternating current (AC) or RF mode must be used to prevent build-up of electron on the substrate surface.

There are a few developments on the research of sputtered CCTO thin film from year 2016. The parameters studied were thin film thickness variation (Ahmadipour et al., 2016a), different sputtering power (Ahmadipour et al., 2017c; Tripathy et al., 2017b) and annealing temperature (Ahmadipour et al., 2017b). The results of the researches showed that the change in thickness of thin film, sputtering power and annealing temperature can alter the grain size and surface features of the CCTO thin films. The change of grain size has direct effect on the optical and electrical properties of the CCTO thin film. Hence, other parameters that can alter the grain size of CCTO thin film must be studied.

Furthermore, the previous researches of metal oxide thin film showed that the increase of deposition temperature will increase the crystallinity and decrease the resistivity of the thin film (Cho & Kim, 2010; Zhang et al., 2011; Mosbah & Aida, 2012). This is due to the increase of temperature will increase the energy of the deposited atoms, therefore they are able to move and arrange properly and this also help in stress relaxation to release the stress cause by sputtering deposition process. The decrease of resistivity is due to the increase of grain size (less grain boundary).

Therefore, the study of effect of deposition temperature on sputtered CCTO thin film is essential for further understanding the change in properties of CCTO thin film toward temperature.

In addition, there are different type of substrates have been used for CCTO thin film deposition such as $LaAlO_3$ (Nigro et al., 2007b), Pt/Ti/SiO2/Si (Fang & Shen, 2003; Prakash et al., 2008), Al_2O_3 (Ahmadipour et al., 2017a), Indium Tin Oxide (ITO) (Ahmadipour et al., 2017c) and Si_3N_4 (Nigro et al., 2007a). The grain size of CCTO thin film on Al_2O_3 and ITO was in the range of 30 nm to 35 nm but the grain size of CCTO thin film on $LaAlO_3$ was in the range of 100 nm to 150 nm. However, there is no explanation about the effect of substrates onto the structural and surface morphology of the CCTO thin film can be found and the actual effect of type of substrates on CCTO thin film still unknown. Hence the further study of CCTO thin film is needed in order to make it more reliable in application such as humidity sensor, capacitor and gas sensor (Löhnert et al., 2015)

1.2 Problem statement

The CCTO with high ε, low tan δ and phase stability up to 300 °C has led to many potential technological applications such as capacitor, antenna, and gas sensor (Kretly et al., 2003; Felix et al., 2012; Löhnert et al., 2015). Due to highly miniaturization of electronic device size, CCTO thin film was started to develop and the different between properties in pellet shape and thin film CCTO was investigated. Li et al. (2010) and Li (2016) found that CCTO thin films have better properties than pellet shape. This is due to thin film provides better thickness uniformity and porosity. In addition, CCTO film are low fabrication cost and low consumption of electrical power (Li et al., 2010; Li, 2016).

CCTO thin film can be prepared through PLD, MOCVD, sol-gel and RF magnetron sputtering. Within these four technique, RF magnetron sputtering shows advantages of better film uniformity, good adhesion, and high packing density (Swann, 1988; Sankaran, 2016) as well as higher production rate and less toxicity compared to PLD and sol-gel. Hence RF magnetron sputtering was used in this project. However, there was only thin film thickness variation (Ahmadipour et al., 2016a), different sputtering power (Ahmadipour et al., 2017c; Tripathy et al., 2017b) and annealing temperature (Ahmadipour et al., 2017b) have been studied on sputtered CCTO thin film. The results of these studies summarized that change in structural and surface morphology is highly affected the optical and electrical properties of CCTO thin film. Chen et al. (2005), Roumie et al. (2010), Cho & Kim (2010) and Zhang et al. (2012), found that the effect of deposition temperature had highly influenced the grain size of sputtered NiO, V_2O_5, YIG and ZnO thin films. This increase the necessity to study the deposition temperature of sputtered CCTO thin film.

In addition, the huge different in grain size of CCTO thin film on Al_2O_3 and ITO (30 nm to 35 nm) (Ahmadipour et al., 2016a, 2017a) compared to grain size of CCTO thin film on $LaNiO_3$ (100 nm to 150 nm) (Li et al., 2009) was observed. However, there is no explanation on the effect of different substrates on the properties of CCTO thin film, this leave potential field to be explored by scientists. Therefore, a study on the effect of substrates on sputtered CCTO thin film is needed.

Hence, in this study, CCTO thin film will be deposited on ITO, fluorine-doped tin oxide (FTO) and glass substrates by using RF magnetron sputtering. In addition, the deposition temperature was set as 100, 150, 200 and 250 °C. The aim of current study is to investigate how the deposition temperature and the type of substrates influence the structural, surface morphology and optical properties of the sputtered CCTO thin film.

1.3 Research objectives

i. To deposit the CCTO thin films by RF magnetron sputtering on ITO, FTO and glass substrate.
ii. To investigate the changes in structural, surface morphology and optical properties of CCTO thin film with respect to deposition temperatures and type of substrates.

1.4 Scope of study

In this work, CCTO thin films were deposited on different substrates (ITO, FTO and glass) at different deposition temperatures (100 °C, 150 °C, 200 °C and 250 °C) using RF magnetron sputtering technique. The effect of deposition temperatures and different type of substrates on structural, surface morphology and optical properties of RF magnetron sputtered CCTO thin film were investigated. The crystalline structure, surface morphology and surface roughness as well as optical energy band gap of the films were characterized by XRD, AFM, FESEM-EDX and UV-vis spectrophotometer.

1.5 Dissertation outline

This dissertation is organized into five chapters. Chapter 1 covers the background of the study, problem statement and objectives of the research. In Chapter 2, literature review of works related to RF magnetron sputtered CCTO thin film is presented. Research methodology, parameters conducted and characterization are laid out in Chapter 3. Chapter 4 focuses on the results and discussion of the work. Conclusion and recommendations for future work are described in Chapter 5.

CHAPTER 2

LITERATURE REVIEW

2.1 Complex oxide

Complex oxide is also known as transition metal oxides, but they composed of complex ternary and higher-order oxides. Besides, complex oxides pose a more excellent properties such as ferroelectrics, colossal dielectric permittivity (ε) and high temperature superconductivity (Liu et al., 2000; Lunkenheimer et al., 2004; Koval et al., 2011). Within transition metal oxides, one family with compounds with chemical formula ABO_3 has received a disproportionate amount of attention from the researchers. ABO_3 is perovskite in structure as shown in Figure 2.1. The excellent properties of the ABO_3 is due to A and B sites able to support metal cations with wide range of valence electrons and size. Hence, this group able to maintain same crystal structure even with doping of different cations and there is no other materials group able to show such characteristic (Zubko et al., 2011). In Figure 2.1, perovskite structure can be explained in terms of close packing AO_3 layers and B site cations occupy all the 6 oxygen and resultant of BO_6 octahedral structural.

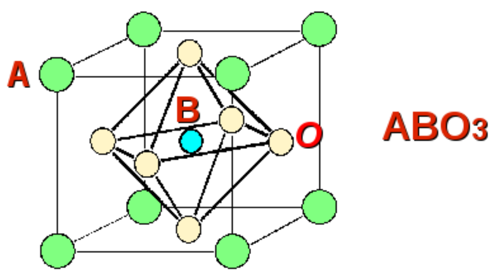

Figure 2.1: ABO_3 perovskite structure (Zhang et al., 2016b)

2.1.1 Calcium Copper Titanate (CCTO)

In the microelectronic era, a material with giant ε value is required to reduce the size of electronic components for the advancement of technology. Other than the giant ε, substantially low tan δ is necessary for the effective performance of these electronic components. Due to these factors, a great number of theoretical and experimental researches have been carried out to develop high ε and low tan δ metal oxide. However, most of the high ε are ferroelectric in nature. High ε property of ferroelectric materials is temperature-dependent accompanying lattice phase transition. This problem limiting the materials in the application as electronic devices (Podpirka, 2012). Therefore, this lead to the research on the materials with giant ε and low tan δ with high temperature phase stability.

CCTO is the materials have giant ε (10,000) and low tan δ about 0.15 at a broad frequency region as well as high temperature phase stability up to 300 °C (Kretly et al., 2003; Felix et al., 2012; Löhnert et al., 2015), hence it fulfill the criteria of advancement technology. CCTO is discovered in year 2000 (Subramanian et al., 2000). They discovered that CCTO belongs to the family of $ACu_3Ti_4O_{12}$ (A = Ca, Sr, Ba, $Bi_{2/3}$, $Y_{2/3}$, $La_{2/3}$)-type oxide of pseudo-cubic perovskite-related structure (space group: Im-3) with a lattice parameter of 7.391 Å. CCTO has the chemical formula of $CaCu_3Ti_4O_{12}$. In addition, CCTO is also an inorganic transparent n-type band gap metal oxide semiconductor with optical energy band gap of 0.34 eV. This value is comparable to band energy of many metal oxide (Pandey et al., 2013).

2.1.2 CCTO structure

CCTO has an ideal cubic perovskite structure by superimposing a body-centered ordering of Ca^{2+} and Cu^{2+} ions share in the A-site as shown in Figure 2.1 (Adams et al., 2006). The crystal structure of CCTO is shown in Figure 2.2. The different in size of Ca^{2+} and Cu^{2+} causes the remarkable tilting of TiO^{6+} octahedra and leading to a body-centered cubic supercell of space group Im-3. Consequently, the Ti^{4+} ions have engrossed centrosymmetric position in the octahedral sites. Tilting also significantly changes the coordination environments of the A-site cations which lead to a 4-coordinate square-planar environment for Cu and a 12-coordinate icosahedral environment for Ca. It is the mismatch in size and the bonding preferences of these two ions and the titanium that drive the huge octahedral tilting distortion. The Ti^{4+} cations could be displaced off center along their one–three fold axis. However, this cannot be a pure ferroelectric transition, because the displacements occur along four different directions. Thus, CCTO has a perovskite-type structure where ε is increased by tension on the Ti-O bonds (Subramanian et al., 2000).

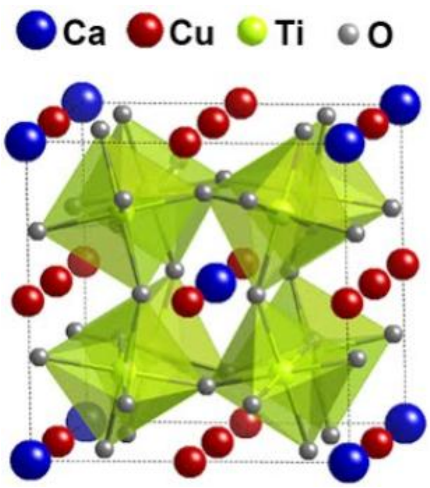

Figure 2.2:Crystal structure of CCTO compound (Varshney & Kumar, 2015)

2.2 Synthesis of CCTO

In order to produce an excellent properties CCTO electroceramic, suitable synthesis methods must be used. Along the development of CCTO, different synthesis methods have been adopted by various researchers in order to tailor its dielectric properties. The synthesis methods are solid-state reaction method (Wang et al., 2013), wet chemistry method (Liu et al., 2007), sol-gel method (Wang et al., 2014), combustion synthesis technique (Ahmadipour et al., 2012), sonochemical-assisted process (Patra, 2009) and co-precipitation methods (Harvey, 2000). The materials required, particle size produced, advantages and disadvantages of the synthesis techniques were showed in Table 2.1. Within these techniques, solid-state reaction method is used mostly in the synthesized of CCTO (Wang et al., 2013; Liu et al., 2015). The common precursors used were $CaCO_3$, CuO and TiO_2 for being mixed with suitable liquid (acetone or ethanol), using ball mill. The chemical reaction during synthesis CCTO using solid-state reaction method is shown in Equation (2.1).

$$CaCO_3 + 3CuO + 4TiO_2 \rightarrow CaCu_3Ti_4O_{12} + CO_2 \uparrow \tag{2.1}$$

To produce a high quality CCTO compound, a proper, standard and repeatable process must be created. The systematically flow chart of solid-state reaction method is shown Figure 2.3 based on Ahmadipour et al. (2016b).

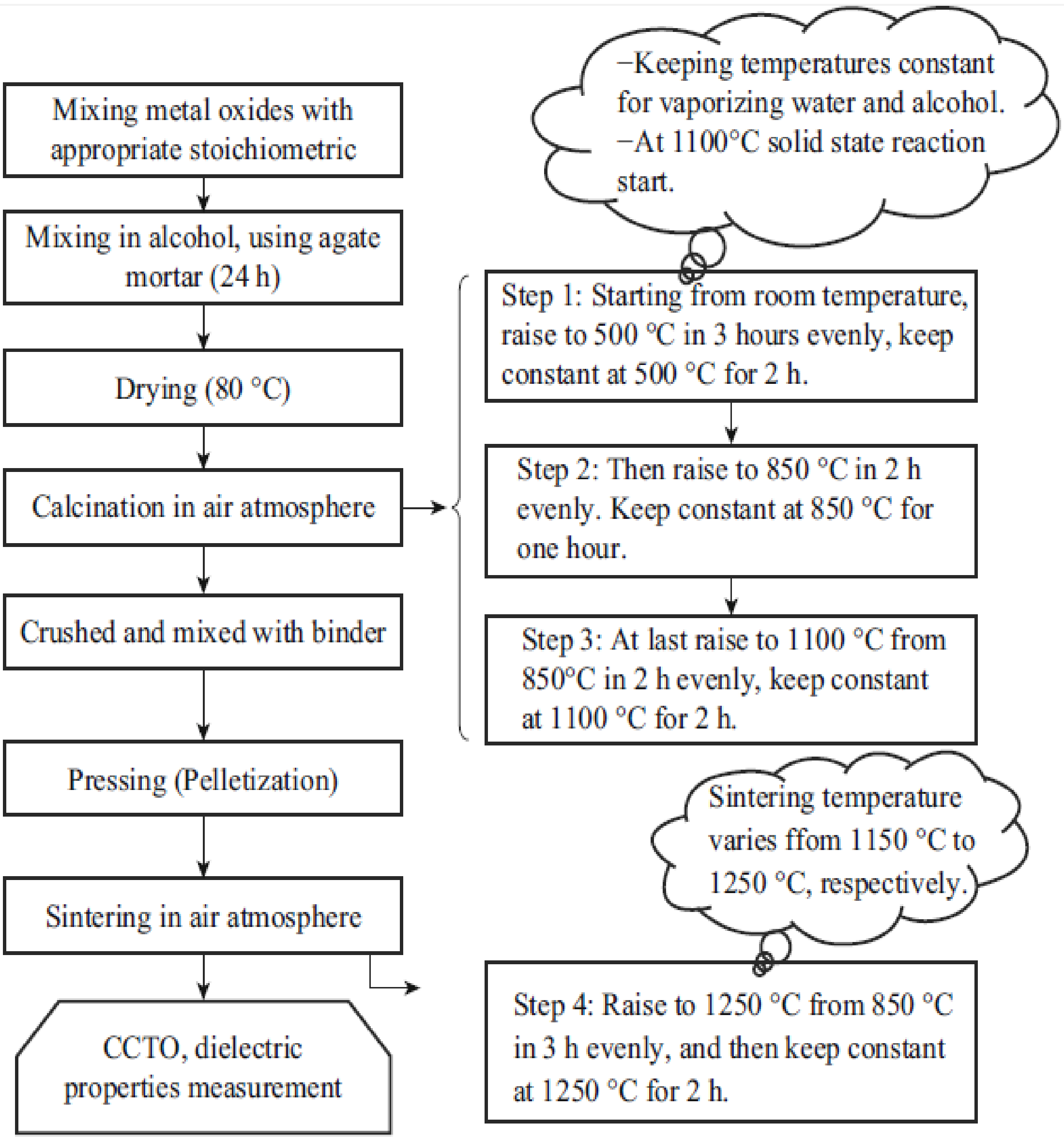

Figure2.3: Systematically flow chart of solid-state reaction method to produce CCTO (Ahmadipour et al., 2016b)

Table 2.1:Various routes for the CCTO synthesis (Ahmadipour et al., 2016b)

Method	Material	Particle size	Advantage	Disadvantage
Solid-state	$CaCO_3$, TiO_2, CuO	3 µm	Produced large amounts Easy to carry out the Synthetic procedure Starting materials readily available	Requires relatively long reaction High temperature condition Secondary phases appear
Wet-chemistry method	$Ca(NO_3)_2 \cdot 4H_2O$,$Cu(NO_3)_2 \cdot 2.5H_2O$, $Ti[OCH(CH3)_2]_4$, citric acid, Acetylacetone, ethylene glycol	4-15µm	Low cost, reliability High Throughput Excellent Selectivity	Very hard to control critical feature dimension Hazardous and Difficult to handle Toxic Fume
Sol–gel	$Ca(NO_3)_2 \cdot 4H_2O$, $Cu(NO_3)_2.4H_2O$, $CH_3OCH_2CH_2OH$,Ti Sol	50 nm	Lower temperatures for processing Can be used to make nanostructured powders, films, fibers	Starting materials are very expensive
Sol–gel	$Ti(OC_4H_9)_4$, $Ca(OOCCH_3)_2{\cdot}H_2O$ $Cu(OOCCH_3)_2{\cdot}H_2O$	260 nm		
Combustion synthesis method	$TiO(NO_3)_2$, $CaCO_3$, citric acid, NH_4NO_3	189-300 nm	Low cost and low temperature process, rapid process Better control of stoichiometry Possibility of multicomponent oxides with single phase and high surface area Exothermic reaction makes product almost instantaneously	Contamination due to carbonaceous residue, particle agglomeration, poor control on particle morphology
Sonochemical-assisted	$Ca(NO_3)_2.4H_2O$ $Cu(NO_3)_2.3H_2O$ Ti $[C_{12}H_{28}O_4]$	75 nm	Nonhazardous, rapid in reaction rate produces very small metal particles	Easy to combine with oxidation or advanced
Co-precipitation	$CaCl_2$, $TiCl_3$ $CuCl_2{\cdot}2H_2O$ Ethanol, oxalic acid used	-	Useful tool for sampling, purifying solutions, and cleaning up environmental hazards. Homogeneous mixing of reactant precipitates reduces the reaction temperature.	It is not suitable for the preparation of high pure, accurate stoichiometric phase. It does not work well, if the reactants have very different solubility as well as different precipitate rate.

2.3 Advantages of thin film over pellet CCTO

In recent years, researches have given considerable focus on the development of materials that can be applied in the solar cell (Kushwaha et al., 2016), gas sensor (Felix et al., 2016), humidity sensor (Ahmadipour et al., 2017a), capacitor (Yao et al., 2016) and so on. For all these microelectronic applications, CCTO thin film was used instead of pellet. The reason behind was CCTO thin films have better properties than pellet shape. For example, from the research of Li et al. (2010) and Li (2016) on humidity sensor, they stated that the pellet shape CCTO have long response and recovery time compared to CCTO thin film. This is due to CCTO thin film have better uniformity and porosity. Furthermore, the researchers also emphasized that the major drawbacks of using pellet-shaped humidity sensor are high pressure/ temperature, time consuming preparation process, and an insufficient porous surface that leads to the decrease of the sensor performance. In addition, the other advantages of film type CCTO are low fabrication cost, low consumption of electric power and more active surface area. All these advantages make CCTO thin film become more promising detector and microelectronic devices.

2.4 Classification of thin film's depositions

The complex oxide thin films are subject of scientific studies because they represent immense promise for 21st century solid state devices (Khadher et al., 2016). Although in the past these materials have been used as bulk materials for many applications, but production of thin film form of these oxides makes them more attractive for various applications. Over the years, considerable progress has been made toward development of various processes for deposition of metal oxide thin film. Almost all of these deposition techniques can be divided into three categories which are physical vapour deposition (PVD), chemical vapour deposition (CVD) and vacuum evaporation (Jameel, 2015). Figure 2.4 shows the organization chart of deposition methods. The excellent properties of epitaxial oxide films cause many extensive reviews on the deposition technique.

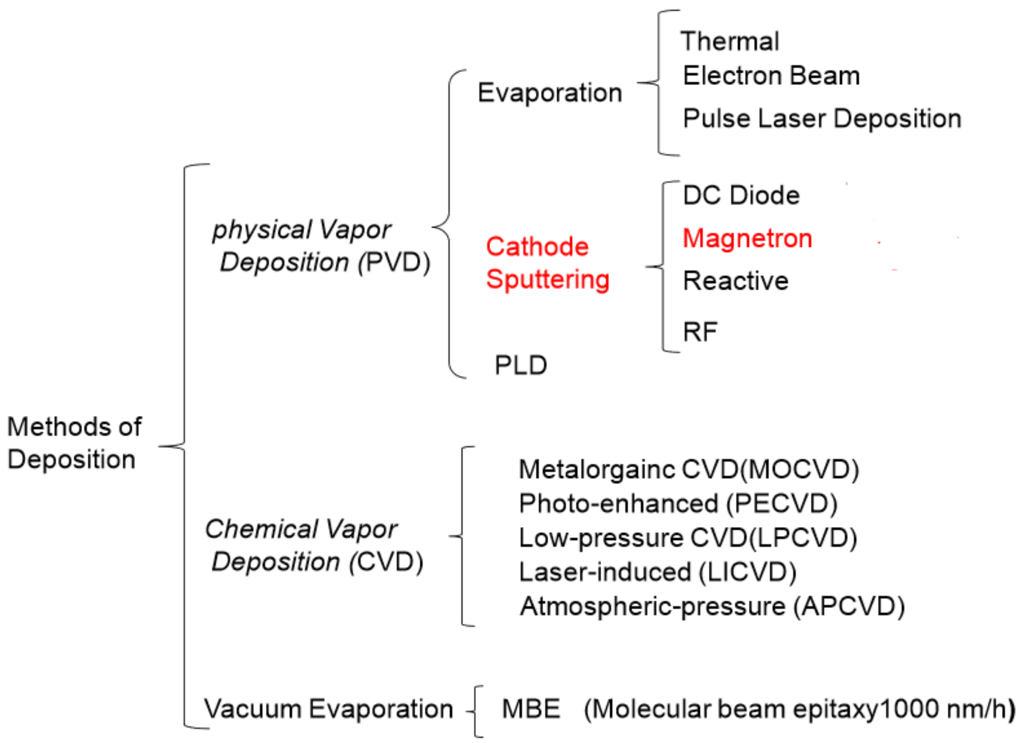

Figure 2.4: Organization chart of deposition methods (Jameel, 2015)

2.5 Deposition techniques of CCTO thin films

Many researchers focused on the preparation of CCTO thin films (Si et al., 2002; Li et al., 2003) due to their unusual dielectric properties and potential applications for microelectronic devices. The relationship between the dielectric properties and microstructures of the deposited thin films was studied in terms of the different substrates via PLD (Fang & Shen, 2003; Zhao et al., 2003; Deng et al., 2007), RF magnetron sputtering (Prakash et al., 2008), MOCVD (Nigro et al., 2007b, a) and sol–gel (Feng et al., 2006; Jin et al., 2007; Maurya et al., 2008). From the studies, there are reliable results were reported for CCTO films prepared by physical deposition methods as PLD. For this technique, ε was measured to be 6000 for epitaxial films, 2000 for polycrystalline thin film. The tan δ values reported for these techniques were in the range of 0.5–0.2 for PLD. Compared to chemical solution deposition methods and sputtering technique, results of PLD are very good, but PLD techniques used are very expensive and complex with time-consuming procedures (Christen & Eres, 2008). Within the chemical solution deposition methods, the sol–gel (Li et al., 2008; Li et al., 2009) and MOCVD have been the most preferred methods used to prepare CCTO thin films. However, for sol-gel technique, highly toxic solutions, doping strategies or buffer layers must be used in order to obtain a good value of ε and tan δ. Consequently, the mechanism of dielectric property of CCTO thin film become more complicated.

Consequently, sputtering has several advantages like low cost, uniformity, ease of synthesis, low temperature processing, non-toxic nature is more preferable in recent study (Tripathy et al., 2017a). However, there is the limited development of sputtering technique using to preparation the CCTO thin film compared to PLD, MOCVD and sol-gel. This can be proved by no research has studied on the effect sputtering parameters such as deposition temperature, gas flow rate and pressure on the properties of sputtered CCTO thin film. Therefore, this leave a potential field to explore.

2.6 Sputtering

Sputtering has become a widely accepted and high demand process for the deposition of thin films since the need for alloys with stringent stoichiometric limits, conformal coverage, and better adherence, for magnetic and microelectronic materials (Kaloyeros & Arkles, 2000). In current technology, there are many ways to deposit materials such as ceramic, metal and plastic onto substrates to generate a thin film. However, sputtering is one of the most common and easily understand process among all the deposition processes. Sputtering is a momentum transfer process between the sputter gas and target atoms (Manova et al., 2010). When a surface is bombarded with high velocity positive ions (sputter gas), it is possible to cause ejection of the surface atoms. Common sputtering gas used is Argon. Then, the ejected atoms can be made to condense on a substrate surface at an optimal distance from the target to form a thin film. The general concept of the sputtering is ejecting atoms from target and condensing the ejected atoms onto a substrate in high vacuum environment. Sputtering process can be run in direct current (DC) or RF mode (insulator must be run in RF mode).

2.6.1 Physical mechanism of sputtering

Figure 2.5 shows the general physical mechanism of sputtering process. In sputtering process, plasma was first created in the sputtering chamber. The positive ions in the plasma are accelerated and form an elastic collision on the surface of target, result of generation of vapours (ejected atoms from target). Typically, the species used for the bombardment is Ar^+ due to lower cost and chemically inert (Kern, 2012).

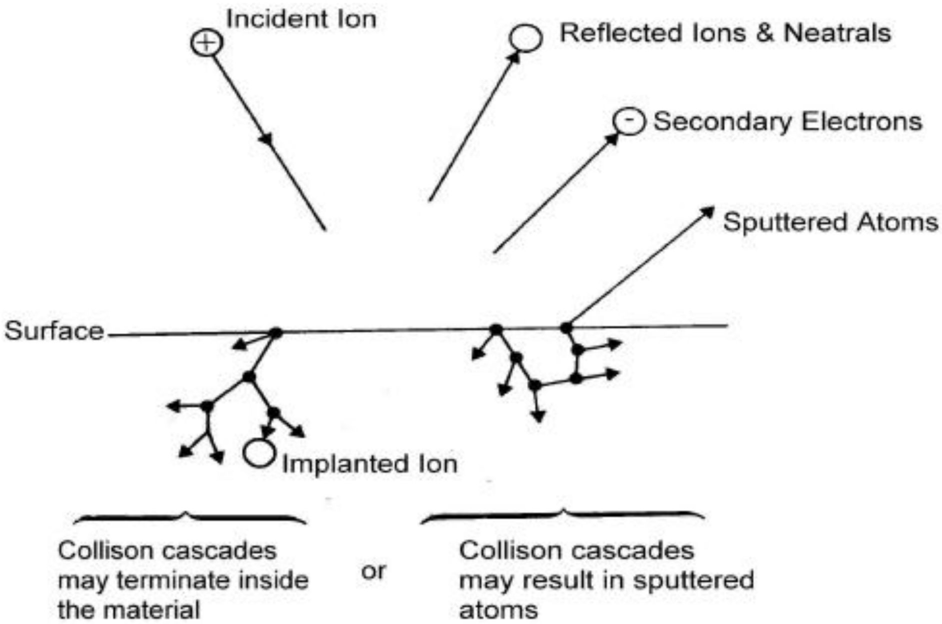

Figure 2.5: Physical mechanism of sputtering (Chapman, 1980)

Once the positive ions (bombardment ion) collides the target surface, atoms can be ejected if the positive ion have enough kinetic energy. Besides, these atoms must successfully go through a cascade of collision in the depth of 5 to 10 nm from the surface of target in order to be ejected, then the ejected atom will condense and deposit on the substrate surface (Kern, 2012). and then thin film is formed.

In addition, there are number of other ions or surface interaction. One of which is the generation of the secondary electrons. These secondary electrons are moved in high speed and collided with the plasma causing further ionisation collision. However, the majority of the electrons produced will not be involved in the ionisation collision but escape to the anode and cause the process rather insufficient (Bunshah, 1994).

Based on the physical mechanism of the sputtering process, the sputtering yield is a measure of the number of the atoms ejected from the surface of target by the bombardment ions. Hence the sputtering process yield is depend on (Mahan, 2000):

- Type and binding energy of the target atoms
- The nature of bombardment ions (inert or reactive gas and mass)
- The energy of the bombardment ions
- Angle of incidence of ions
- Relative mass of ions and atoms

The energy of the bombardment ion must exceed a certain threshold in order for the sputtering to become possible. This threshold is approximately four times the binding energy of the materials to be sputtered (Mattox, 1998).

2.6.2 DC/ RF sputtering

The sputtering technique is classified into two main categories which are DC or RF depending on the type of power supply used. Figure 2.6 (a) shows the schematic diagram of DC sputtering system. DC sputtering is mainly used to deposit metal thin films. The reason of DC sputtering not suitable for insulator is due to after the ions strike the surface, their charge will remain localized on the target, after a passage of time, the positive charge will build up on the target surface, hence make the target unfeasible to further bombard by ions (Manova et al., 2010). This issue can be prevented by using RF potential to the target.

RF potential provide an oscillating voltage to the target to cause ionizing collisions and maintained the self-sustained discharge. In addition, since electrons is lighter than ions hence they have higher mobility compared to the ions. Consequently, higher number of electron will reach the insulating target surface during the half positive cycle compared to positive ions during the half negative cycle. This build up a negatively charge on the target surface hence repels the electrons around the target and form an ions sheath. This enriches the positive ions in front of the target surface and increase the ions bombard on the target and sputtering is achieved. In RF sputtering, the most general frequency used is 13.56 MHz (Todorow, 2009). Lastly, the most important difference between DC and RF is RF requires an impedance matching network between sputtering chamber and power supply (Todorow, 2009). Figure 2.6 (b) shows the schematic diagram of RF sputtering.

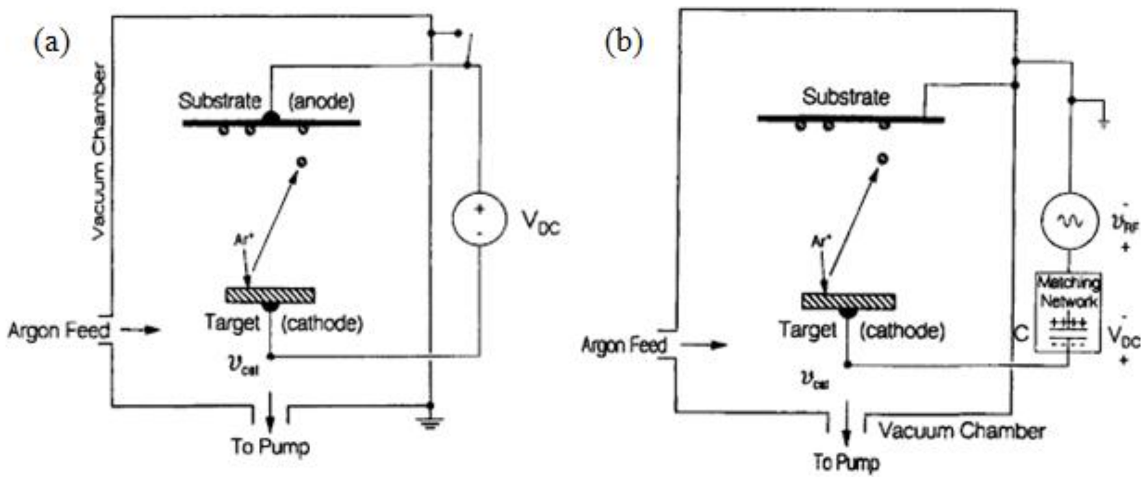

Figure2.6 : Schematic of (a) DC and (b) RF sputtering system (Kurdesau et al., 2006)

2.6.3 Magnetron sputtering

Magnetron gun used in the sputtering process will utilize the strong magnetic fields to confine charged plasma particles close to the surface of the sputter target in order to increase the sputter yield (Depla et al., 2010). With the applied of magnetron, magnetic field line is created and electrons movement will follow the magnetic field line (helical path) (Bosco et al., 2012). This increase the effective path length of electrons therefore causing more ionizing collision with the sputtered gas near the target surface. Sputtered gas normally is Ar since it is inert in nature. With the ionisation collision with electrons, the Ar^+ ions are formed and bombarded on the target surface. High number of Ar^+ ions bombarded on the target surface and produce many ejected atoms from the target. Ejected atoms are mostly neutral in nature and also much heavier, hence they not be affected by magnetic field (Depla et al., 2010). Used of magnetron sputtering will increase the deposition rate of the sputtering process.

In addition, applied of magnetron is more important for RF sputtering than DC sputtering (Depla et al., 2010). This is due to electrons RF sputtering are presented at the space between target and substrate, therefore they probably do not have enough energy to cause the ionisation collision. With the applied of the magnetic field, it will constrain the electrons near to target and hence improve the RF discharge efficiency. Schematic of RF magnetron sputtering system is shown in Figure 2.7.

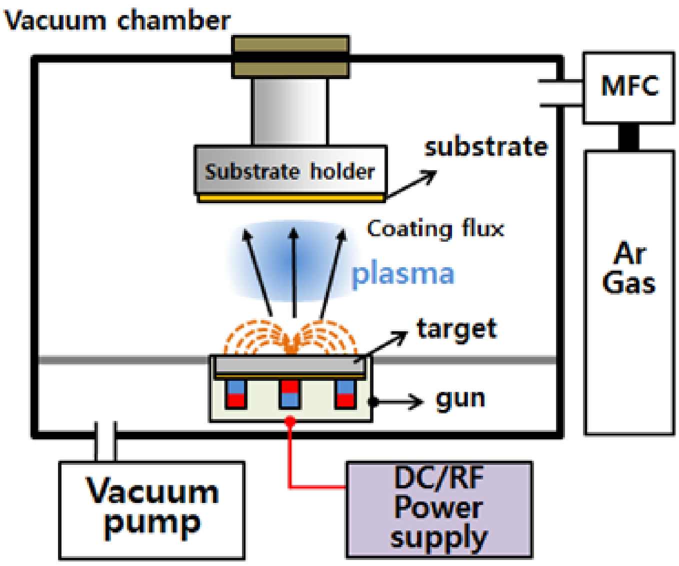

Figure 2.7:Schematic of RF magnetron sputtering system (Bosco et al., 2012)

2.6.4 Advantages of sputtering over other deposition methods

In sputtering process, the entire surface of the target is the source while for evaporation process only a point where the electron beam hit on the target become the source of deposition. Hence the surface source implies a higher and better coverage during sputtering compared to evaporation deposition technique (Depla et al., 2010). Furthermore, the ejecting atoms bombard the substrate surface with high kinetic energy able to rearrange themselves and then condense on the substrate. This gives a better adhesion to the substrate. Furthermore, due to the high kinetic energy of sputtered atoms, redistribute on the surface of the substrate, result of a high uniformity, density, constant thickness thin film and able to deposit over larger surface area. Lastly, with incorporating target cooling provision in sputtering process, higher melting point element can be deposited (Riekkinen et al., 2002).

2.6.5 Parameters affecting sputtering process

The parameters that can affect the deposition process of thin film are base vacuum, sputter gas pressure during deposition, sputter power, gas flow rate and deposition temperature. The quality of the sputtered thin film such as microstructure, surface roughness, adhesion, density and crystallinity are highly depended on the above parameters. Since there are such large number of parameters in sputtering process, this definitely make the process complicated. On the other hand, if the parameters are optimized properly, it provides the advantage of large degree of control over the thin film growth (Schneider & Lippert, 2010). Besides, deposition geometry which is the relative orientation of the target and substrate also plays an important role that affect the thin film deposition process. Hence, the parameters of the sputtering process must be studied properly so that optimum parameters can be used to produce a high quality thin film.

2.7 Studies of sputtered CCTO thin film

Since CCTO has giant dielectric permittivity and negligible temperature dependence on the dielectric permittivity hence it is suitable for microelectronic applications (Ramirez et al., 2000; Subramanian et al., 2000; Sinclair et al., 2002). Due to the miniaturization of the electronic device demand, CCTO thin film is needed to produce and to be integrated to the semiconductor technology (Tripathy et al., 2017a).

RF magnetron sputtering has been used for deposition of many type of thin films and it able to provide high uniformity for large-area processing, strong adhesion and long-term stability of thin film. However, there is only a few researches on the sputtered thin film. Ahmadipour et al. (2016a, 2017a), and Li et al. (2009) had studied the effect of the sputtered CCTO film thickness on structural, surface morphological and optical properties of CCTO thin film on Al_2O_3, ITO and $LaNiO_3$ substrates respectively. From the studies, increases of the surface roughness, grain size and decreases of optical energy band gap were detected as the thin film thickness increase. Besides, the grain size of CCTO thin film on $LaNiO_3$ substrates (100 nm - 150 nm) was three to five times bigger compared to grain size CCTO thin film on Al_2O_3 and ITO substrates (30 nm - 35 nm). Hence, even though the effect of thickness is properly understood, but the direct comparison of the effect of substrates is not available.

Besides, the effect of RF sputtering power has been studied by Tripathy et al. (2017a) and Ahmadipour et al. (2017c). Whereas the increase in RF sputtering power showed increase in grain size, surface roughness and also optical energy band gap. The change of Ra and optical energy band gap is mainly due to the grain size, structure and crystallinity of the thin film. Furthermore, effect of annealing temperature on the CCTO thin film had been studied (Ahmadipour et al., 2017b). Increase of annealing temperature was significantly increase the grain size, Ra and decrease the optical energy band gap of CCTO thin film. The decrease in optical energy band gap is mainly due to the increase of grain size and reduce of grain boundary density (Cho & Kim, 2010).

Besides, from the studies, the optical energy band gap variation of CCTO thin film are closely related to crystal structure (especially grain size) and microdefects in the thin films (Vetterl et al., 2002). While the grain size, structure and crystallinity are highly depended on and can be controlled by the sputtering parameters. In addition, the reported XRD database for sputtered CCTO thin film were ICDD data card no.98-005-8088 (Ahmadipour et al., 2016a, 2017a, 2017c) and JCPDS 75-2188 (Felix et al., 2012). So far there is no a specific report study on effect RF magnetron sputtering parameters (deposition temperatures) on CCTO thin film properties.

2.8 Importance of deposition temperature in sputtering

Sputtering is a low temperature deposition process and only small fraction (~ 1%) of the total applied energy is consumed in the process of ejecting of the sputtered particles and secondary electrons. Most of the energy is consumed by the ions to move and strike the cathode or target. The ejecting atoms with a certain amount of energy will move, condense and deposit on the substrate surface. Hence, a considerable amount of energy is dissipated at the target and substrate. In order to increase the sputter yield, a