Chapter 2

Theoretical Background

The theoretical aspects related to the deposition of zinc oxide thin film and its properties will be discussed in this chapter. The RF magnetron sputtering, which is the method of thin film preparation in this research, will be also explained for some details on the important principles, i.e. the sputtering system itself, the mechanisms and the film formation by this process.

2.1 Zinc Oxide Thin Films

2.1.1 Zinc Oxide Properties

Zinc oxide (ZnO) is a II-VI compound semiconductor material with wide and direct band gap of wurtzite structure. The crystal structure is depicted in Fig. 2.1. ZnO is optically transparent in visible wavelength region due to a large band gap, $E_g \gtrsim 3$ eV [19]. The properties of ZnO can be summarized in Table 2.1. ZnO is naturally n-type semiconductor, the electrical conductivity can be improved by intrinsic (defects) or extrinsic (dopants) charge carriers.

If ZnO thin film is prepared intrinsically, i.e. without intrinsic or extrinsic donors, its resistivity is very high (on the order of $\gtrsim 10^7$ $\Omega \cdot$cm) [19]. ZnO with perfect crystal structure behaves as an insulator. Thus, low resistivity ZnO thin film which is required for the application such as transparent electrodes can be achieved in two ways. One way is the creation of intrinsic lattice defects which
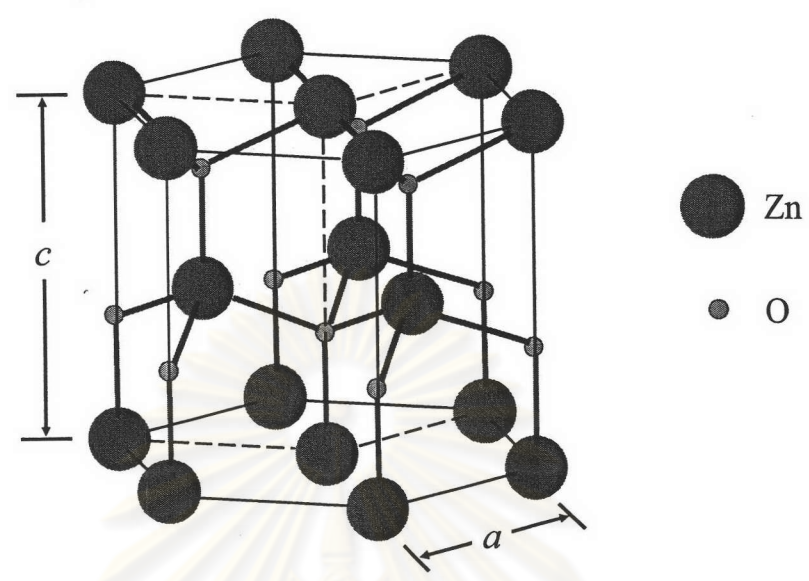
Figure 2.1: Wurtzite structure of ZnO.

Property	ZnO
Mineral name	zincite
Bandgap E_g (eV)	3.3
Melting point (°C)	1975
Heat of formation (eV)	3.6
Density (g cm^{-3})	5.67
Relative permittivity	8.1
Effective electron mass m^*/m_e	0.28
Dopants	B, Al, In, Ga, Si, Sn, F, Cl
Crystal structure	hexagonal, wurtzite
Lattice paremeter (Å)	a: 3.250, c: 5.207
Thermal expansion α (300 K) (K^{-1})	∥ c: 2.92, ⊥ c: 4.75

Table 2.1: Properties of the ZnO material [19]

are oxygen vacancies or zinc interstitial atoms. Another way is the introduction of extrinsic dopants which are usually metal atoms in group III elements on zinc lattice sites.

2.1.2   Defects and Dopants in Zinc Oxide Structure

Usually the crystal structure of prepared ZnO thin films is not perfect, but contains imperfections or defects. The majority defects being the intrinsic donors are oxygen vacancies and zinc interstitial atoms. They are schematically shown in Fig. 2.2 at (1) and (2), respectively. An oxygen atom may be missing from a particular site. This defect is referred to as an oxygen vacancy. In another situation, a zinc atom may be located between lattice sites. This defect is thus called a zinc interstitial atom. These defects affect to the electrical properties because they play the role as dopants from imperfection in thin film. The conduction characteristics of non-doped ZnO are primarily dominated by electrons generated by oxygen vacancies and interstitial zinc [2, 19]. These properties exhibited by ZnO thin films depend on the non-stoichiometry of the films, resulting from the presence of oxygen vacancies and zinc interstitial atoms [1, 2]. Both defects can be called intrinsic donors.

However, non-doped ZnO usually presents a high resistivity because of a low carrier concentration. Thus, the introduction of impurity atoms or extrinsic dopants, as shown in (3) of Fig. 2.2, is important in order to improve the electrical properties of the ZnO thin film. Impurities or dopants can be located at normal lattice sites of zinc in which case they are called substitutional impurities. An effective way to decrease the resistivity of the film is by doping with donor atoms. The electrical behavior of the ZnO thin films can be improved by doping with group III elements, which have higher number of valence electrons. Group III elements, such as B, Al, Ga and In, are well known to act as an effective n-type dopant in ZnO [16, 20]. Then, the resistivity in the doped ZnO film can be lower than that of pure ZnO film due to the increase of carrier concentration from these dopants known as extrinsic donors.
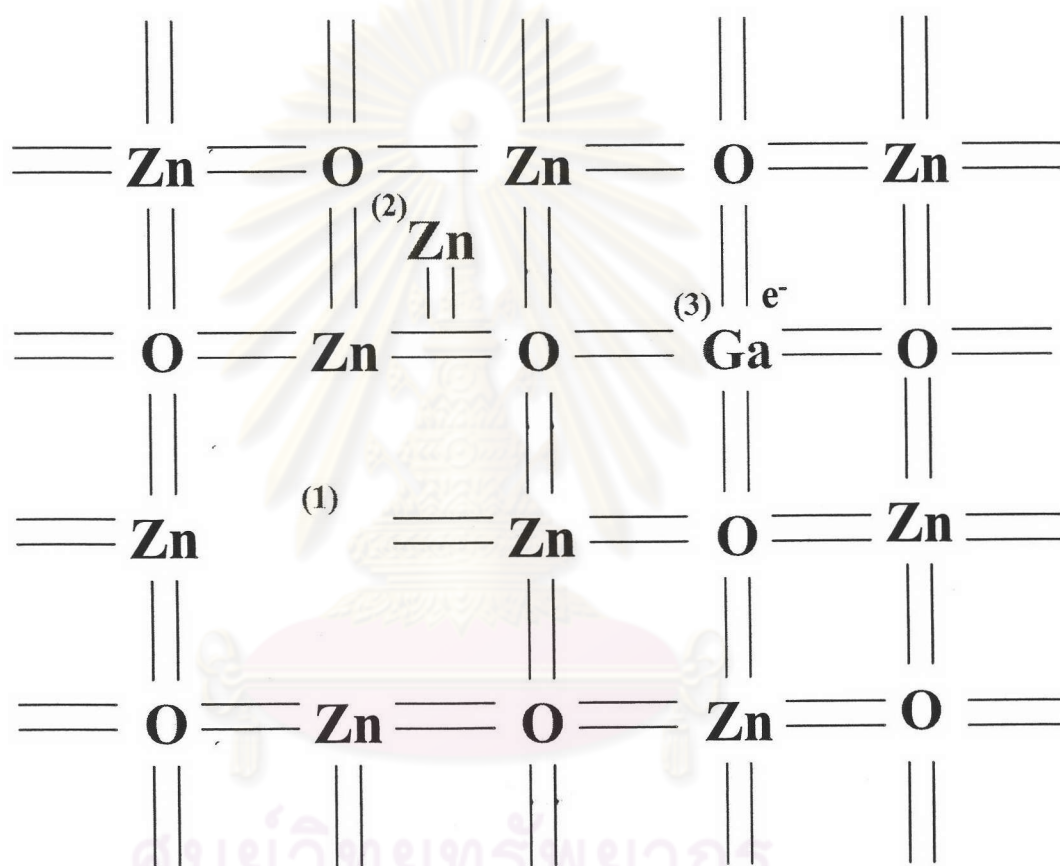
Figure 2.2: Two-dimensional representation of the ZnO lattice showing (1) an oxygen vacancy, (2) a zinc interstitial atom and (3) a substitutional gallium dopant

2.1.3 Ga-Doped Zinc Oxide (GZO) Thin Films

The most common dopants are elements from group III. Al has been mostly used. Nevertheless, Al presents a very high reactivity leading to oxidation during the growth process, with a deterioration of the electrical properties [20]. Ga is somewhat less reactive and more resistant to oxidation compared to Al [14, 17, 20]. Recently, Ga doping is more interesting because of its electrical and optical properties and Ga-doped ZnO (GZO) thin film is suitable for use as transparent conductive oxide (TCO) in several optoelectronic devices.

In addition, a damp-heat test, which measures the change of thin film properties under high relative humidity and temperature for a long time, of the sputtered Ga-doped ZnO films was carried out [13, 18]. It was found that the films had good stability of electrical properties and showed a very small change of sheet resistance compared to B-doped ZnO thin films prepared by MOCVD technique. Moreover, GZO thin film was confirmed to have better humidity resistance than AZO by measuring the change of sheet resistance after lefting outdoors for two months in winter [18]. Furthermore, it was found that the deformation of ZnO lattice is minimized in the case of high Ga concentrations [14]. These are the main reasons why Ga has been chosen as a dopant.

2.2 Principles of Sputtering

Sputtering is perhaps the most preferable technique for the deposition of ZnO thin films due to its capability to deliver high deposition rate on large area substrates [21, 22]. In addition, the ZnO thin films prepared by this technique are also nontoxic and relatively easy to fabricate. Sputtering is a physical vapor deposition (PVD) process involving the removal of materials from a solid cathode. This is achieved by bombarding the cathode with positive ions emitted from a gas discharge. The subsequent collision knock loose, or sputtered, atoms from the material when ions with high kinetic energy are incident on the cathode. The process of momentum

transfer from impacting ions to surface atoms forms the basis of sputter coating. Sputtering was developed to deposit refractory metals or materials, which could not be deposited using the thermal evaporation techniques [23]. Today, sputtering has been developed into a versatile deposition technique that is able to deposit wide range of materials.

2.2.1 Plasma Glow Discharge

Glow discharge is the sustained phenomenon that atoms or molecules are ionized by electrons containing external energy [24]. Plasma glow discharge process can be produced by supplying high voltage to the two electrodes in vacuum chamber. The simplest sputtering for understanding is the DC glow discharge sputtering. The simplified sputtering system is shown in Fig. 2.3. The target is a plate of materials to be sputtered. It is connected to the negative terminal of a DC power supply, then the target is also known as the cathode which is applied by high voltage $(3-5$ kilovolts). The substrate that faces the cathode is grounded and generally called the anode. Both electrodes are parallel in the vacuum chamber. After evacuation of the chamber, gas, typically argon, is introduced as the medium in which a discharge is initiated and sustained.

When the voltage is applied to the cathode, the electric field is generated between the electrodes. A very small current flows at first because of the small number of initial charge carriers that are primary electrons from stimulation by cosmic ray in the system. As the voltage is increased, the energy is imparted to charged particles to create more carriers. This occurs through ion collisions with the cathode that release the secondary electrons, and by impact ionization of neutral gas atoms. The current increases rapidly with charge multiplication but the voltage, which is limited by the power supply, remains constant. The voltage in this regime is called "breakdown voltage (V_B)" and this regime is known as the "Townsend discharge", as shown in Fig. 2.4. Large number of electrons and ions are created through avalanches. When enough of the electrons generated produce sufficient
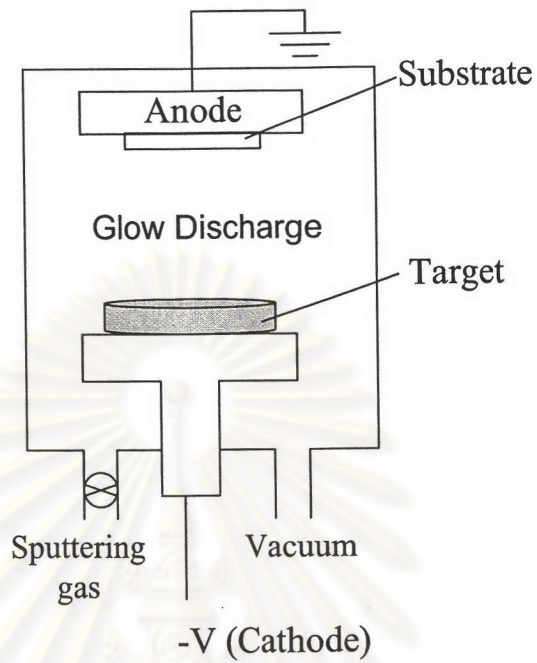
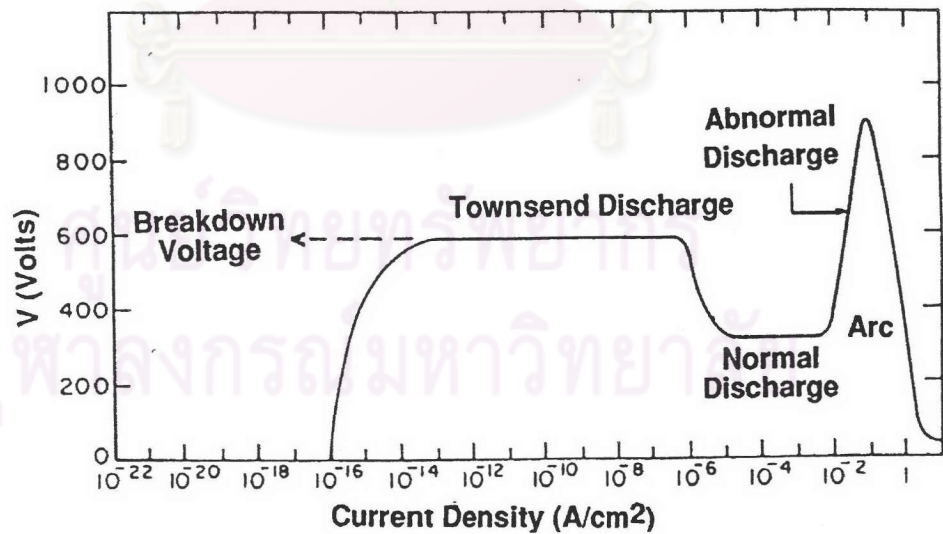Figure 2.3: Schematic of simplified DC sputtering system

Figure 2.4: The relationship between the current density and voltage of DC glow discharge system [25]

ions to regenerate the same number of initial electrons, the discharge becomes self-sustaining. The gas begins to glow and the voltage drops, accompanied by increasing of current. This stage is called "normal glow" regime. When more power is applied, the bombardment of the cathode increasingly spreads over the whole surface until a nearly uniform current density is achieved. The increasing power results in higher voltage and current density. This enters into the "abnormal discharge" regime that is an operative domain for sputtering process because of high discharge current density and the ability to be controlled directly by power supply. However, the low-voltage will decrease dramatically at higher currents due to thermionic electron emission.

2.2.2 Collision Processes

Collisions between electrons and charged or neutral species within the plasma dominate the properties of the glow discharge. Collisions are elastic or inelastic, depending on whether the internal energy of colliding species is preserved. In an elastic collision, the billiard ball model is exemplified that only kinetic energy is interchanged. This collision can be explained by conservation of momentum and kinetic energy of translational motion. There is no atomic excitation and the potential energy of the colliding species, which basically resides within their electronic structure, is conserved. Therefore, only the kinetic energy is considered in the calculation. From the elastic binary collision, as shown in Fig. 2.5, the result is [24]

$$\frac{E_t}{E_i} = \frac{4M_i M_t}{(M_i + M_t)^2} \cos^2 \theta, \tag{2.1}$$

where i and t refer to the two particles of mass $M_{i,t}$ and energy $E_{i,t}$. Assume M_t is initially stationary and M_i collides at an angle θ defined by the initial trajectory and the line joining their centers at contact. The quantity $4M_i M_t/(M_i + M_t)^2$ is known as the energy transfer function. Consider a collision between a moving electron and a stationary gas molecule ($M_i << M_t$), then little kinetic energy is transferred in the collision of the light electron with massive gas atom.
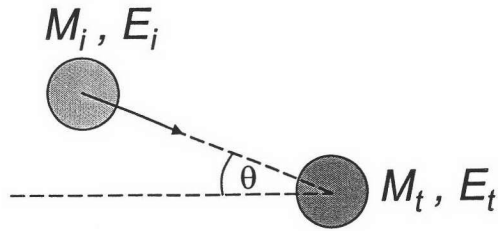
Figure 2.5: Schematic depiction of the binary collision

Consider inelastic collisions, the change in internal energy (ΔU) of the particle M_t which is struck by an incoming particle M_i must be explained in the condition requiring conservation of total energy. The fraction of kinetic energy of particle M_i that can be transferred to the internal energy of particle M_t has a maximum value of [24]

$$\frac{\Delta U}{(1/2)M_i v_i^2} = \frac{M_t}{(M_i + M_t)} \cos^2 \theta,$$
(2.2)

where v_i is the initial velocity of the particle M_i. For the inelastic collision between an electron and gas molecule and $\cos \theta = 1$, all of an electron's kinetic energy can be transferred to the heavier species. The glow discharge environments contain electrons, various of ions, neutral atoms and molecules, and photons. Inelastic collision involving electrons are dominant in determining the behaviour of the glow discharge. These important processes can be shown as the followings [24, 26].

Ionization. The most important process in sustaining the glow discharge is electron impact ionization. A typical reaction is

$$e^- + Ar \longrightarrow Ar^+ + 2e^-.$$
(2.3)

The primary electron removes an electron from the atom, and then the positive ion and two electrons are produced. The two electrons can produce more ionization. By this multiplication process, a glow discharge is maintained.

Recombination. It is the reverse reaction of ionization process. An electron combines with the positive ion to form an excited neutral ion.

$$e^- + Ar^+ \longrightarrow Ar^*.$$
(2.4)

Excitation. In this process, the energy of bound electron jumps to a higher energy level within the atom which is collided by an incoming electron. The energy of incoming electron is not enough to ionize a neutral atom. However, it has enough energy to excite a bound electron in an atom from the ground state to the excited state.

$$e^- + Ar \longrightarrow Ar^* + e^-. \tag{2.5}$$

Relaxation. The electron in the excited (unstable) state returns to the ground state in this process. Each transition is accompanied by the emission of a photon (γ) of which energy equals the difference in energy between the states.

$$Ar^* \longrightarrow Ar + \gamma. \tag{2.6}$$

This process happens suddenly after the recombination or excitation process. One of the immediately self-evident features of a glow discharge is that it glows. This glow is due to the relaxation of excited atoms or molecules. The frequency of photon depends on energy level of electron and type of gas.

The above four basic inelastic collision processes are used to explain the glow discharge. Furthermore, there are some other collision processes and some of these are important under certain situations, however they are not paid attention in this chapter.

2.3 Sputtering Processes

2.3.1 Ion-Surface Interactions

The analysis and design of sputtering process is an understanding of what happens when ions collide with the surface of target [24, 26]. Some of the interactions and the effects of energetic particles on a surface target that occur are shown schematically in Fig. 2.6 [19]. Each interaction depends on the type of ion, mass, charge, the nature of the surface atoms involved and ion energy. The ion may be reflected, probably
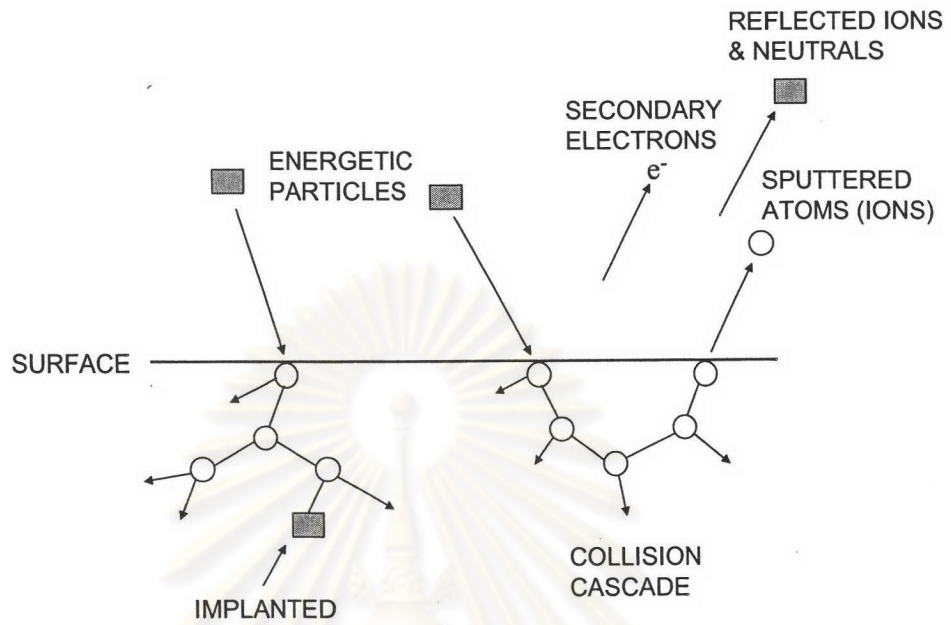
Figure 2.6: Depiction of energetic particle bombardment effects on a solid surface [19, 24]
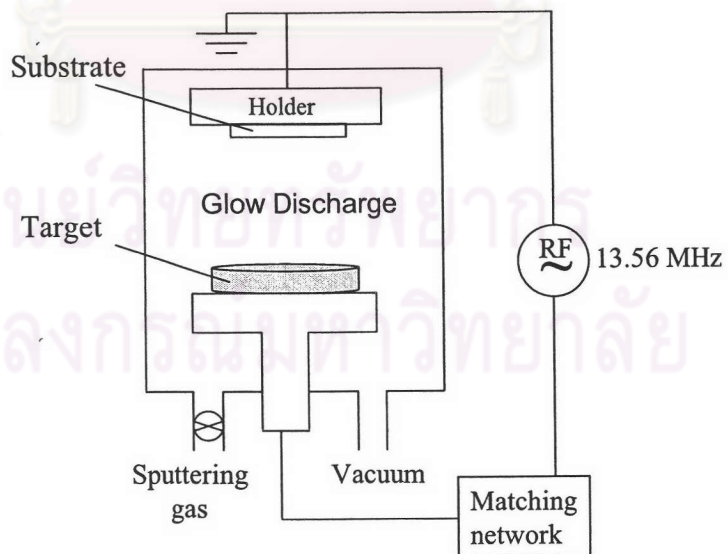

Figure 2.7: Schematic of simplified RF sputtering system

being neutralized in the process or implanted in the target. The electrons, usually called as the secondary electrons, can be ejected from the target by the impact of ions. The ion impact may also be responsible for some structural rearrangements in the target material. It may also set up a series of collisions between atoms of the target, leading to the ejection of one of these atoms. This ejection process is known as sputtering. Several of these interactions have been widely used for thin film deposition, processing and characterization techniques [24].

2.3.2 RF Sputtering

When the targets composed of insulators or dielectrics are sputtered, they will build up significant positive charges resulting in the collection of positive ions that cannot be drained away. As a result, RF sputtering was developed to deposit insulating thin films. The RF sputtering system is depicted schematically in Fig. 2.7. Consider what happens when an ac signal is applied to the electrodes. At high frequencies, the electrons oscillating in the glow region acquire enough energy to cause ionizing collisions, reducing the need for secondary electrons to sustain the discharge. In general, RF sputtering uses a 13.56 MHz sinusoidal voltage to drive the source. It is a frequency allotted by international communications authorities at which one can radiate a certain amount of energy without interfering with communications [26]. The substrate and chamber walls are held at ground potential. As the RF signal is applied to the target, a large initial electron current is drawn and the charge that builds up on a dielectric target is dissipated through the positive half of the cycle. However, only a small ion current flows during the second half of the cycle. The RF system is the need for a matching network and RF power supply. The matching network is needed to match the impedance of the supply to the chamber in order to maximize the power transfer from the power supply to a load or target.

2.3.3 Magnetron Sputtering

In the sputtering system, the magnetron sources can be used to increase the ionization of sputtering gas and generated electrons. A magnetic field controls the motion of the electrons. The plasma glow discharge increases due to the change of path of electrons under the magnetic field. The deposition rate is also improved because of the increasing of plasma density.

Parallel Magnetic and Electric Fields

Consider what happens when a magnetic field $\overrightarrow{B}$ is superposed on the electric field $\overrightarrow{E}$ between the target and substrate. Electrons within the dual fields experience the Lorentz force [24]

$$\overrightarrow{F} = \frac{m d \overrightarrow{v}}{dt} = -q(\overrightarrow{E} + \overrightarrow{v} \times \overrightarrow{B}), \tag{2.7}$$

where q, m and v are the electron charge, mass, and velocity, respectively. The electrons are only influenced by the $\overrightarrow{E}$ field when they are emitted exactly normal to the target surface and parallel to both fields. If an electron is launched from the cathode with velocity v at angle θ with respect to $\overrightarrow{B}$ and $\overrightarrow{E}$, it experiences a force $qvB\sin\theta$ in a direction perpendicular to $\overrightarrow{B}$. The electron moves in a helical path with a radius of $r = mv\sin\theta/qB$. The pitch of the helix lengthens with time because of electron acceleration in the $\overrightarrow{E}$ field, as shown in Fig. 2.8. The magnetic field prolongs the electron residence time in the plasma and thus enhance the probability of ion collisions. This leads to larger discharge currents and increases deposition rates.

Perpendicular Electric and Magnetic Fields

In magnetrons, electrons ideally do not even reach the anode but are trapped near the target, enhancing the ionization [24]. This is accomplished by employing a magnetic field oriented parallel to the target and perpendicular to the electric field,
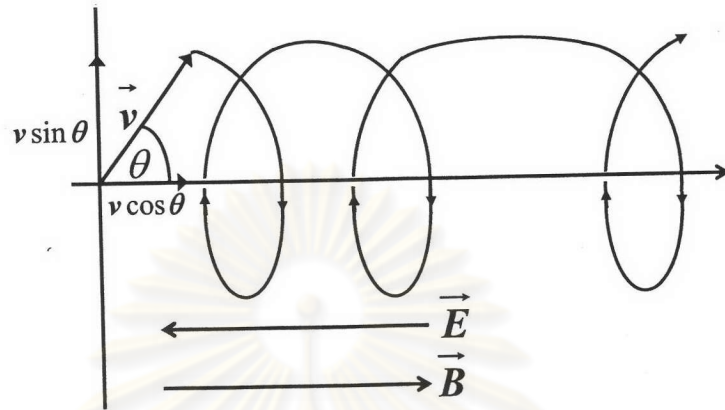
Figure 2.8: Effect of parallel magnetic field $\overrightarrow{B}$ and electric field $\overrightarrow{E}$ on electron motion [24]
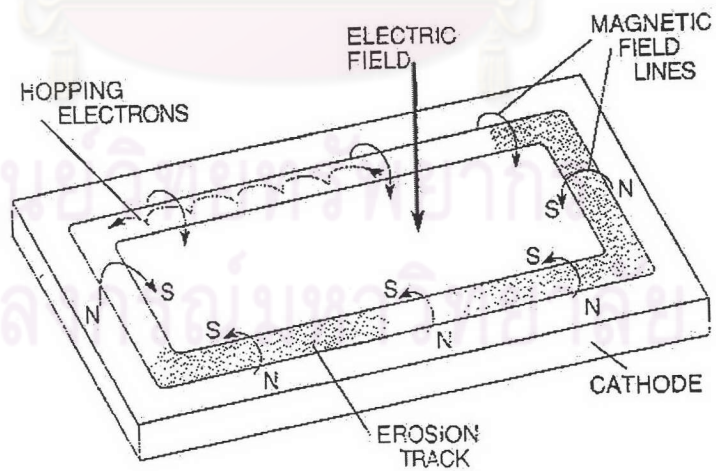

Figure 2.9: Applied fields and electron motion in the planar magnetron [24]

as shown schematically in Fig. 2.9. For example, this is practically achieved by placing permanent bar, ring or horseshoe magnets behind the target with the south pole at the center of the target and the north pole in a band at the edge of the target. Hence, the magnetic field lines first emanate normal to the target, then bend with a component parallel to the target surface and finally return to complete the magnetic circuit. Electrons emitted from the cathode are initially accelerated toward the anode, moving in a helical motion, but they are bent in an orbit back to the target in the same way. The resulting magnetic field confines the electrons to a circular path on the surface of the target. By suitable orientation of the target magnets, the target erosion by sputtering occurs within the track where the electrons hop around at high speed because ionization of the working gas is very intense above it.

2.4 Thin Films Deposition by RF Magnetron Sputtering

2.4.1 The System of RF Magnetron Sputtering

A typical RF magnetron sputter deposition system, as shown schematically in Fig. 2.10, mainly consists of a vacuum chamber, pressure guages, a sputtering source with magnetrons, a matching network, a substrate holder and a pumping system. Deposition pressure is controlled by the rate of gas passing into the chamber. By adjusting the gas flow into system, a constant pressure can be maintained. The pumping system may be the combination of a turbo molecular pump, or a diffusion pump and a rotary pump. The inert gas, usually argon gas, is then ionized by using high potentials at the source. The RF power supply is used for this glow discharge system.
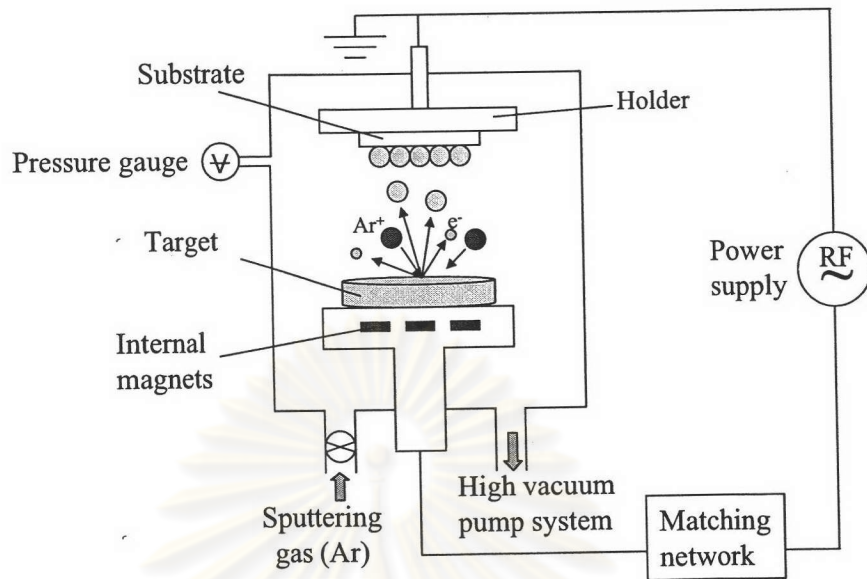
Figure 2.10: Schematic of RF magnetron sputtering system

2.4.2 The Mechanisms of Sputtering

The sputtering is a deposition of thin film under glow discharge system. The large difference in potential between the electrodes forms a plasma, caused by ionization of the argon atoms. This ionization results in a negatively charged electron and positive ion pair, whereas the plasma retains a net neutral charge. The positive charged ions are attracted to the target and accelerated by the electric field, resulting in a collision with the target material. The surface of target is bombarded by high energetic ions or ionized gas atoms, leading to sputtering of the target atoms. They receive momentum and kinetic energy from ionized ions, and then they can move out of the target surface. Thus, the target atoms can be formed a coating on the substrate.

2.4.3 Sputtering of Compound Materials

In this research, all samples were prepared by sputtering of ZnO target which is the compound material target. Thus, the sputtering of a chemical compound target is
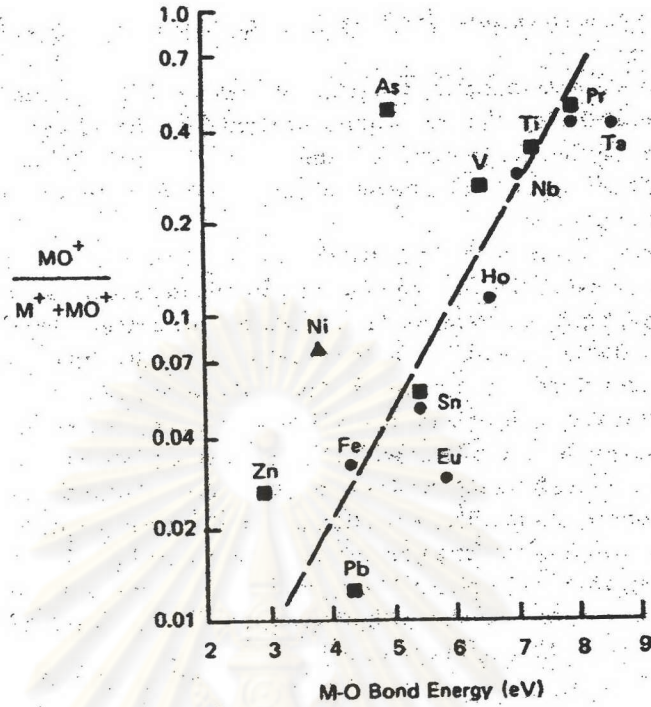
Figure 2.11: The dependence of $MO^+/(M^+ + MO^+)$ on the bond energy M-O [26]

considered. This target is sputtered as both molecular species and atoms. In the RF sputtering of metal oxides, the relative numbers of metal oxide molecular ions can be given by [26]

$$\eta = \frac{MO^+}{(M^+ + MO^+)}, \tag{2.8}$$

where MO^+ is numbers of metal oxide molecular ions, M^+ is numbers of atomic metal ions. It can be seen that η is strongly influenced by the relevant $M - O$ bond strength, as shown in Fig. 2.11. More strongly bonded metal oxide ions are less likely to be disassociated. The η value is defined and measured to underestimate the relative concentration of the sputtered molecular ion. Figure 2.11. shows that the ratio of zinc oxide molecular ion is quite low because the bonding energy is small. Thus, most species sputtered from the ZnO target are atomic ions.

2.4.4 Thin Film Formation

In sputtering deposition, material arrives at the substrate mostly in the form of atoms or molecules. The deposited atoms diffuse around the substrate with a motion determined by its binding energy to the substrate [26]. The energetic atoms will move or jump into adjacent sites on the substrate. After a certain time, an atom will join with another diffusing single atom to form a doublet, which is less mobile but more stable than the single atom. The chance of forming the atomic pair will depend on the single atom density and deposition rate. In time, the doublets will be joined by other single atoms to form triplets, quadruplets and so on. This is the "nucleation stage" of thin film growth, leading to the formation of quasi-stable islands. Each island contains tens or hundreds of atoms. During the "island growth stage", the islands grow in size rather than in number. They grow large enough to touch each other. This is the "coalescence stage". There are often crystallographic reorientations as a result of competition between the structures of the coalescing islands. Coalescence proceeds until the film reaches continuity, but this may not occur in some cases until the film is several hundred angstroms in average thickness. Figure 2.12. shows the stages of thin film formation.

If surface atoms are mobile, they have a greater opportunity of finding low energy positions, consistent with crystal growth, in the growing film. It also takes time to find an energetically favourable lattice position. Crystal growth is also encouraged by low deposition rates. During the island stage of polycrystalline films growth, each island will contain one or a few crystallites. The low deposition rate leads to large grains, low density of crystal defects and large uniform film [26]. The structure of the growing film is found to be extremely sensitive to deposition conditions.
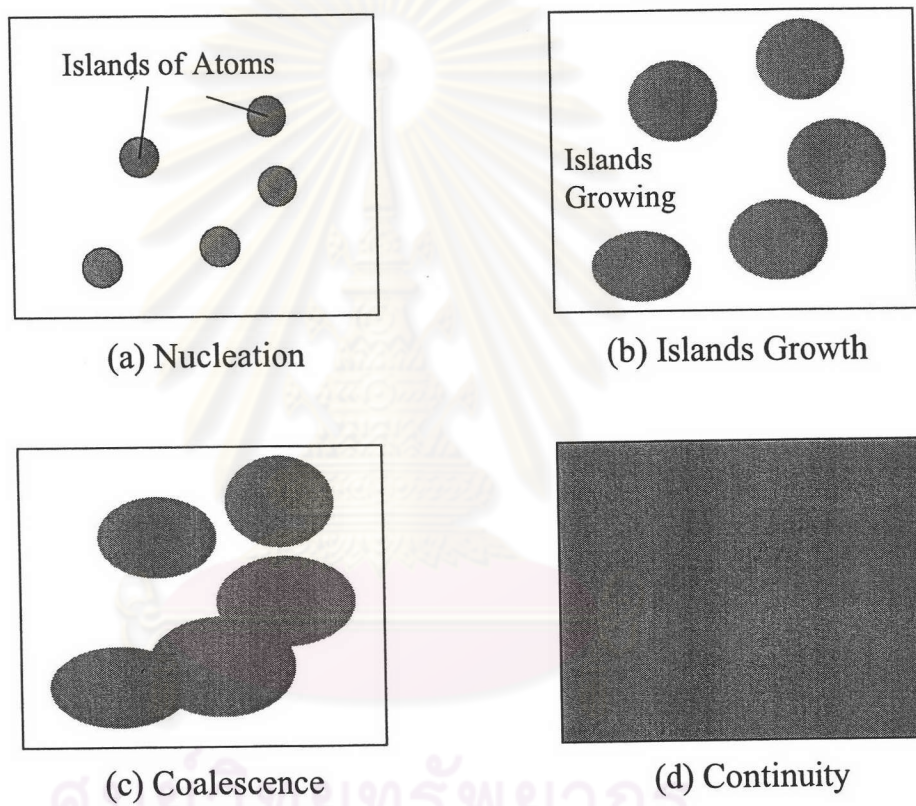
Figure 2.12: Formation of a thin film [26]