CHAPTER II

THEORETICAL BACKGROUND

2.1 Cr$_x$N Thin Films

There are two type of chromium and nitrogen compound: Cr$_2$N and CrN, which are hexagonal and cubic structure, respectively. These two structures are shown in Figure 2.1. The hexagonal structure Cr$_2$N and the NaCl structure CrN have the lattice parameter 4.805 Å and 4.140 Å, respectively.
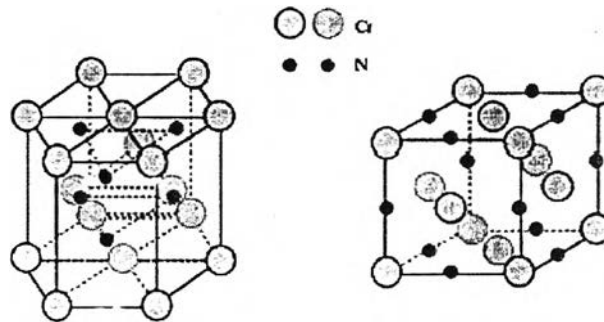

Figure 2.1: Schematic of crystal structure for (a) hexagonal Cr$_2$N and (b) cubic CrN [17]

For comparison between Cr$_2$N film and CrN film, Cr$_2$N film has higher hardness than CrN film [18]. For the adhesion of the film, CrN film has better adhesion than Cr$_2$N film [18, 19]. In addition, the friction coefficient of CrN film is lower than Cr$_2$N film [19].

Figure 2.2 shows phase diagram of the Cr-N system and their corresponding microstructure as observed by XRD [10]. In the range of the growth temperature from 0 °C to 250 °C, the stability of β-Cr$_2$N varies from 30.3 to 33.3 at % N. The two-phase region of Cr$_2$N and CrN follows the region of homogenous Cr$_2$N.
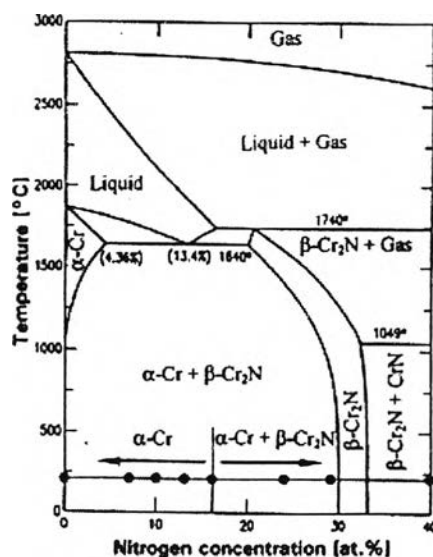
Figure 2.2: Phase diagram of the Cr-N system and their corresponding microstructure as observed by XRD [10]

There are many works that studied the structural and tribological properties of chromium nitride thin films in the past 20 years.

In the 1980s, Aubert et al [20] studied mechanical properties of magnetron-sputtered chromium coatings. The results showed that only α-Cr phase could be detected and concluded that these coatings could be used for wear resistance application.

Cosset et al. [21] studied the structure, corrosion, adhesion, hardness and wear of magnetron sputter $Cr_{1-x}N_x$ coatings with x = 0–0.11 at the deposition temperature between 200 °C and 500 °C. They concluded that the properties of coatings depend on the deposition temperature and nitrogen content in the films.

Berg et al. [18] studied Cr-N films deposited by reactive r.f. magnetron sputtering. The results showed that pure hexagonal Cr_2N structure, which was dominated by nitrogen flow rate within a small set of parameters. The hardness value could be defined in form of the universal hardness under test force (HU) and the plastic part of the universal hardness after reloading (HU_{pl}). HU and HU_{pl} of Cr_2N film were 11.3±0.9 GPa and 26.8±0.7 GPa, respectively at maximum growth temperature 195 °C. In contrast, HU and HU_{pl} of CrN films were 10±1.2 GPa and 23.2±4 GPa, respectively at maximum growth temperature 170 °C. This was due to CrN films had a columnar structure and Cr_2N films had a dense structure.

Gautier et al. [22] studied the influence of substrate temperature and bias voltage on the formation of Cr-N phase. Substrate temperatures were varied between 200 °C and 500 °C. Bias voltages were varied between 0 and 200 V. In this work, Cr_xN films were deposited by magnetron sputtering and vacuum arc evaporation techniques. The results showed that there was a mixing of Cr_2N + CrN at lower nitrogen pressure and the single CrN films were occurred at higher nitrogen pressure in vacuum arc evaporation technique. However, CrN was the only structure that can be occurred in the magnetron sputtering technique. Evolution of the texture coefficient was happened when the bias voltage was varied. Texture developed from (111) to (220) at higher bias voltage. For both techniques, the microhardness of films increased as the substrate temperature increased. This was due to the mobility of adatoms increased as the substrate temperature increased. This phenomenon leaded to more perfect structure. For arc evaporation, the texture changed preferred orientation from (220) to (111). Because <110> direction was preferred sliding direction, the microhardness of (220) texture was lower than others. For magnetron sputtering, grain growth was more important with an increasing of the substrate temperature than for arc evaporation. In contrast, ion bombardment in the magnetron sputtering had less importance than that in the arc evaporation. Futhermore, the energy of adatoms was not high enough to avoid the columnar growth, which was well known to develop bad mechanical properties. These two reasons leaded to less microhardness in sputtering films than in evaporation films. In addition, the films from both techniques showed the same wear depth and tended to decrease with an increasing of substrate temperature. The microhardness of sputtered film at 250 °C was about 14 GPa.

Rebholz et al. [9] studied the influence of nitrogen content in reactive magnetron sputtered $Cr_{1-x}N_x$ on structural, mechanical and tribological properties. The films were grown at substrate temperature about 200 °C on AISI 316 stainless steel in Ar/N_2 variation. The results indicated that an amount of nitrogen in the films was a function of nitrogen flow rate. For $Cr_{1-x}N_x$ with x = 0–0.16, only the α-Cr phase could be detected. In addition, $Cr_{1-x}N_x$ with x = 0.1–0.16 showed good adhesion and the best wear resistance. The hardness increased from 700 up to 2400 $HK_{0.025}$ as the nitrogen in the films increased. The maximum hardness of $Cr_{1-x}N_x$ thin films was at x= 0.29.

Cunha et al. [23] studied the structural properties and mechanical properties of CrN films that were produced by reactive DC and RF magnetron sputtering. The

influence of bias voltage was investigated. The results showed that CrN films deposited at low substrate bias had texture with [111] planes parallel to substrate. Increasing the bias made the orientation change and (200), (311) and (222) orientations became visibly. The hardness of the films, which were grown at 300 °C and without bias substrate, was 19.3 GPa and tended to increase as the bias voltage increased.

Wei et al [19] studied the nanotribological behavior of DC magnetron sputtered Cr, Cr_2N and CrN thin films using nanoscratch techniques. They concluded that Cr_2N films had the highest hardness and most effective protective coating materials followed by CrN and Cr. However, the adhesion of Cr_2N films had the lowest value. The hardness of Cr, Cr_2N (N_2 partial pressure 8%) and CrN (N_2 partial pressure 20%) was found at 9.3, 16.1 and 12.5 GPa, respectively at room temperature. This was due to excess nitrogen in films that leaded to decrease the hardness and wear resistance.

Xu et al [24] studied the effect of deposition parameters on the composition, structure, density and topography of the films. In this work, CrN thin films were deposited on single crystal silicon substrates by r.f. magnetron sputtering and the N_2 and Ar flow rate were varied. They concluded that cubic- phase could be observed in films with a wide range of nitrogen gas flows. The composition of CrN films was controlled by the flow rate of N_2 and the flow rate ratio of Ar and N_2. The density of CrN films decreased with an increasing of the flow rate at room temperature. This was due to an increasing of the number of collisions between CrN particles and gas atoms. The hardness of films increased at higher substrate temperature. The effect of gas flow rate made the deposition rate decrease when the nitrogen flow rate increased. The surface roughness of the films increased with an increasing of the Ar and N_2 flow rate, as Ar flow rate was the main parameter for the surface roughness.

Fornies et al [1] showed that with an increasing of partial pressure of nitrogen from 2% to 100%, the structure of chromium nitride developed from Cr+N, $Cr+CrN_x$, Cr+CrN to Cr_2N. The hardness value without bias was about 20 GPa with a maximum value of 21 GPa for the nitrogen flow rate at 100% (Cr_2N). Applied bias voltage influenced on the hardness that increased as the negative bias increased. The friction coefficient values were between 0.4 and 0.8 for nitrogen flow rate 40% and 70%. The wear rate values without bias were about 4×10^{-6} mm^3/Nm and 300×10^{-6} mm^3/Nm for the nitrogen flow rate 40% and 70%, respectively.

2.2 Concept of Sputtering

Sputtering is one of the most common methods for the deposition of thin films. The concept of the sputtering process is that atoms of a target are bombarded by energetic ions. There are energy and momentum transfer between ions and atoms of the target. If the energy of target atoms overcomes the surface binding energy, the target atoms are ejected to form a film on a substrate. Figure 2.3 shows a schematic of a basic DC sputtering system. The target is connected to a dc power supply and the substrate can be grounded, biased or floated. The substrate can also be heated to a specific temperature. The substrate is opposite the target. After pumping down the system to the base pressure, sputtering gas, generally inert gas such as Ar gas for non-reactiv sputtering mode is filled. When the negative voltage is applied to the target and the sputtering gas is ionized (Ar $\rightarrow$ Ar$^+$ + e$^-$), the target is then bombarded by positive gas ions. Then, most neutral atoms of the target are sputtered away from the target surface and kinetically move toward the substrate to form a film layer on the substrate.
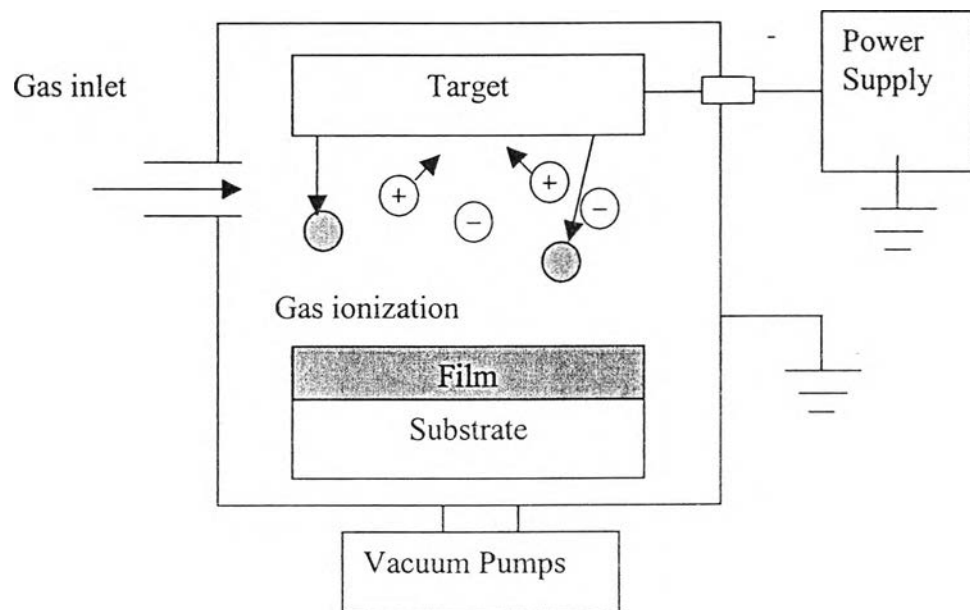

Figure 2.3: Schematic of a basic DC sputtering deposition system

2.3 DC Glow Discharge

DC glow discharge is one of the simplest sputtering techniques. Figure 2.4 shows the relationship between current density and voltage in a DC glow discharge system. When dc power is applied to the target, little current flows due to small number of initial charge carriers (electrons and gas ions). As the applied voltage increases, the gas particles are imparted sufficient energy to create more carriers. The positive ions in the plasma are accelerated to the target (cathode) and then target atoms include secondary electrons are ejected. At the same time, the secondary electrons from the target and ionization ions in the plasma are accelerated to the substrate (anode). As a result, the current is increased rapidly and a "Townsend discharge" is created. This is the beginning of avalanches that a large number of electrons and ions are created. When a number of electrons and ions are produced the same, discharge becomes self-sustaining. Then, glow becomes to increase and accompany with sharp rise in the current and drop in the voltage. This is the "normal glow" state. As more power applied, the bombarded ions are increased over the surface until a nearly uniform current density is achieved. This is the "abnormal glow" state and normal sputtering regime [25].
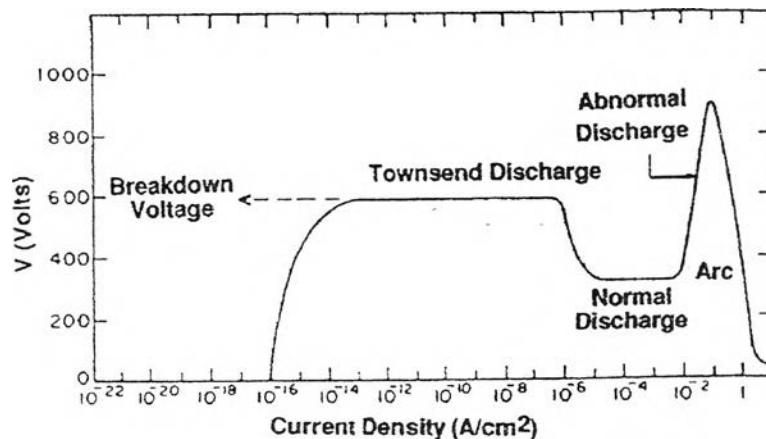

Figure 2.4: The relation between the current density and voltage in a DC glow discharge system [25]

2.4 Ion – Surface Interactions at the Target

When the ions bombard the target, following processes may occur:

a) Ion or neutral atoms are reflected.

b) Secondary electrons are emitted from the target due to ion impact.

c) Sputtered atoms are ejected from the target.

d) The ions are buried in the target with/without the ejection of target atom.

Each interaction depends on the type of ions (mass, charge), the nature of surface atoms and ion energy. The interactions between ions and target atoms lead to the sputtering phenomena. The momentum of energetic particles is transferred to target atoms. The sputtered target atoms can be ejected when collisions occur at a certain number of times. These collisions change the direction of momentum transfer towards the target surface.

Incident Ion

Sputtered Atom

Sputtered Atom

Low Energy Knock-on
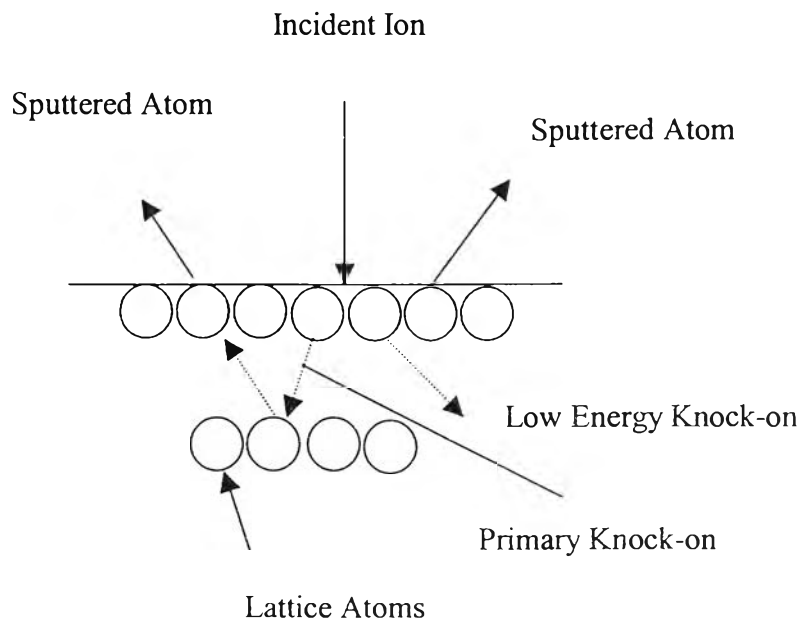
Primary Knock-on

Lattice Atoms

Figure 2.5: Momentum exchange processes at the target [25]

The momentum exchange processes are shown in Figure 2.5 [25]. There are three major events that can occur in the process. The bombardment ions that have a low energy knock-on and transfer their energy to the neighbor surface atoms. Then, sputtered atoms are ejected from the target. Otherwise, the primary knock-on atoms can collide several times inside the target before transferring the momentum that cause sputtering. On the other hand, the primary knock-on atom can itself be reflected and hit the surface atoms.

2.5 Magnetron Sputtering Technique

The basic diode sputtering process has been known for many years and many materials have been successfully deposited using this technique [26]. However, the process is limited by low ionization efficiencies in the plasma and high substrate heating effect. These limitations have been overcome by development of the magnetron sputtering.

Magnetrons are used in the sputtering process to increase the ionization. This technique is known as "Magnetron Sputtering". There are 2 poles of magnet used for magnetic configurations in magnetrons. One pole is at the central axis of the target and the second pole is a ring magnet that is around the outer edge of the target. This confines the magnetic field that parallels to the target surface. The magnetic field can constrict secondary electron motion to the vicinity of the target. This can help the ionization increase.

Suppose the electron with the velocity $(\vec{v})$ travels at an angle θ to the magnetic field $(\vec{B})$. The electron will be forced by a magnitude of $Bev\sin\theta$ perpendicular to the field. If there is no collision, the electron will move with circular motion around $\vec{B}$ at the radius given by

$$\frac{m_e(v\sin\theta)^2}{r} = Bev\sin\theta, \qquad (2.1)$$

$$\text{or} \qquad \frac{m_e v\sin\theta}{Be} = r, \qquad (2.2)$$

coupled with the velocity $v\cos\theta$ parallel to $\vec{B}$, the motion will be a helix.

Trapping the electrons in this way can increase the probability of collisions between electrons and gas. This leads to increase the ionization efficiency and density of plasma in the target region. In addition, the increased ionization efficiency makes the ion bombardment at the target increase and higher sputtering rate than a basic sputtering. Therefore, the deposition rate at the substrate is higher than that of the basic sputtering.
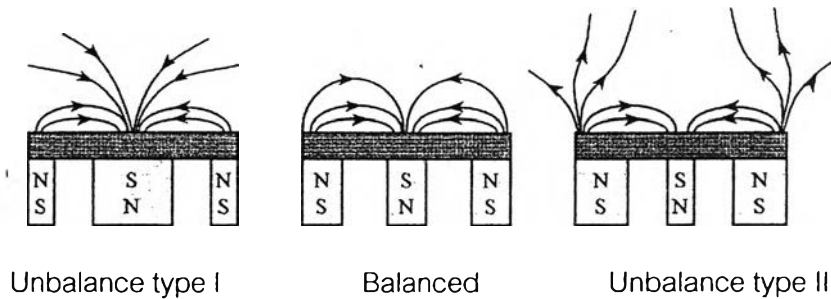

Figure 2.6: Magnetic configurations in magnetron sputtering [27]

The magnetrons can be classified into 3 types according to their magnetic configurations, as shown in Figure 2.6 [27]: balanced magnetron, unbalanced magnetron type I, and unbalanced magnetron type II. In the case of the balanced magnetron, the central and the outer poles are equally strong. The plasma is strongly limited to the target region. If the films grown on the substrate that is in this region, they will be subjected to concurrent ion bombardment. This parameter influences the structure and properties of the films. In the unbalanced magnetron type I, the inner pole is stronger than the outer poles. In this case, the magnetic field lines are directed towards chamber walls and the plasma density in the substrate region is low. This design is not commonly used because of the lower ion current at the substrate. On the other hand, the outer pole is stronger than the central pole in the unbalanced magnetron type II. In this case, the magnetic field lines are not only closed between the central and outer pole, but also some lines are directed towards the substrate. Thus, some secondary electrons can follow these field lines. Consequently, the plasma can flow out of the substrate. High ion current can be extracted from the plasma without the bias substrate. Furthermore, the ion current goes to the substrate and the deposition rate is directly proportional to the target current. As a result, the ion to arrival atom ratio at the substrate remains constant with an increasing of deposition

rate. The unbalanced magnetron type II has been used in the growth of Cr_xN films in this work.

2.6 Reactive Sputtering Process

In sputter deposition with a pure metal target using inert gas, a metal film can be formed. However, if the process contains non-inert gas such as O_2, N_2 and CH_4 as reactive gas, the chemical reaction between the target material and the sputtering gas will occur. This process is called "reactive sputtering" [28]. The metallic target can be sputtered in reactive gas to form a compound thin film. Reactive sputtering also includes sputtering from a compound target. At very high pressure some reactions between sputtered atoms and the reactive gas can occur in the plasma. However, at normal sputtering pressure (3-30 mTorr) the chemical reaction generally occurs at the surface. This could be on the target surface or the substrate. When a compound forms on the target, the sputtering rate decreases and the partial pressure of the reactive gas increases rapidly. The target is in "poisoned" state and the material deposited from the poisoned state is different from the non-poison state. This problem can be overcome by using the partial pressure of reactive gas.

During the reactive sputtering, the film may be a solid alloy of the target metal doped with the reactive element, a compound or some mixture of the two. The condition that requires alloy or compound film can be shown in Figure 2.7a [29]. This figure shows the hysteresis curve between the total system pressure (P) and the flow rate of the reactive gas (Q_r) into the system. If the inert gas such as Ar is only one gas in the system, the total pressure will depend on the flow rate of inert gas, as shown in the dotted line. As Q_i increases, P increases due to the constant pumping speed. When the reactive gas such as N_2 is filled in the system, the flow rate increases from $Q_r(0)$. However, the total pressure is constant at the beginning because the reactive gas reacts with the target and removes from the gas phase, as shown in state A. In this state, the film is not formed but the atomic ratio of reactive gas in the metal target increases with an increasing of Q_r. As the flow rate increases to the critical flow rate (Q_r^*), the total pressure increases to new pressure (P_1). If the reactive sputtering were not happened, the pressure would be higher such as P_3. At the equilibrium value of P,

the change in Q_r influences P such that it can be increased or decreased linearly, as shown in state B. If Q_r decreases sufficiently, the pressure reaches the initial pressure.

The transition from state A to state B is happened because of formation of compound on the metal target. When the positive ions bombard on the compound target, the secondary electron emission is much higher than the metallic target. This phenomenon makes the plasma impedance in state B be lower than in state A. And this effect relates the hysteresis of the target voltage with reactive gas flow rate at constant discharge current, as shown in Figure 2.7b [29]

System pressure (P)

(a)

Cathode voltage

(b)

Figure 2.7: Hysteresis curve during reactive sputtering [30] (a) Hysteresis curve for system pressure vs. reactive gas flow rate during reactive sputtering (b) Hysteresis curve of cathode voltage vs. reactive gas flow rate at constant discharge current

2.7 Collision Processes of Two Particles

In plasma, collision between electrons and all other species (charge or neutral) is dominated. Elastic or inelastic collision depends on the internal energy that is preserved. In the elastic collision, all atoms are not excitation. Moreover, kinetic energy and momentum is conserved. This is the reason why only kinetic energy is considered. The result for elastic binary collision is [30]

$$\frac{E_2}{E_1} = \frac{4M_1M_2}{(M_1+M_2)^2}\cos^2\theta,\tag{2.3}$$

where M_1, M_2 and E_1, E_2 are mass and energy of two particles, respectively. Figure 2.8 shows a schematic depiction of the binary collision.
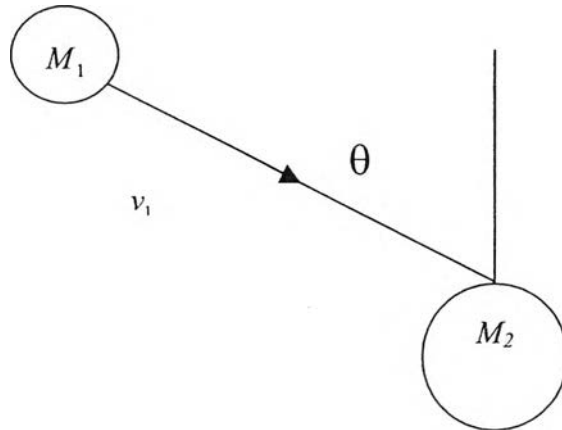

Figure 2.8: Schematic depiction of the binary collision

Let M_2 particle is stationary where M_1 particle collides with velocity v_1 at an angle θ to the line joining the centers of M_1 and M_2 at the moment of the collision. The factor $\dfrac{4M_1M_2}{(M_1+M_2)^2}$ is known as the energy transfer function. For an electron hitting a molecule of gas such as nitrogen molecule, M_1 (electron mass) is less than

M_2 (gas molecule). Therefore, energy transfer function is about $\dfrac{4M_1}{M_2}$. As a result, little kinetic energy is transferred in the collision.

In the inelastic collision, the kinetic energy of electron can be transferred to heavier specie

$$\frac{\Delta U}{\frac{1}{2}M_1 v_1^2} = \frac{M_2}{(M_1 + M_2)^2}\cos^2\theta, \qquad (2.4)$$

where ΔU is the change in internal energy,

v_1 is the initial velocity of particle 1.

2.8 Film Formation of Sputter Atomic Flux

In the film formation process, as shown in Figure 2.9 [30], Sputtered atomic flux arrives at the substrate, as in process A. Then, these adatoms diffuse on the substrate, or they re-evaporate, as in process B. In case of the interaction between the adatoms, they are called "Cluster" which have lower diffusion and more stable than single atoms, as in process C. As more sputtered atoms arrive at the surface, the adatoms form triplets, quadruplets and so on. This is a nucleation stage of thin film growth, as in process D, E and F respectively. Next, the certain size of clusters, which is called "Island", is formed. During the island stage, each island is a single crystal when the substrate is single crystal such as Si. Otherwise, on polycrystalline substrate, the orientation of each island will be random. Therefore, the film is polycrystalline. Each island comes closer to each other and has interaction between clusters. This process is called "Coalescence", as in process G. From an observation in the transmission electron microscope, the island displays liquid - like behavior during coalescence. There is often crystallographic reorientation because of competition between the structures of the coalescing island. The coalescence proceeds until the film reaches continuity, as in process H.
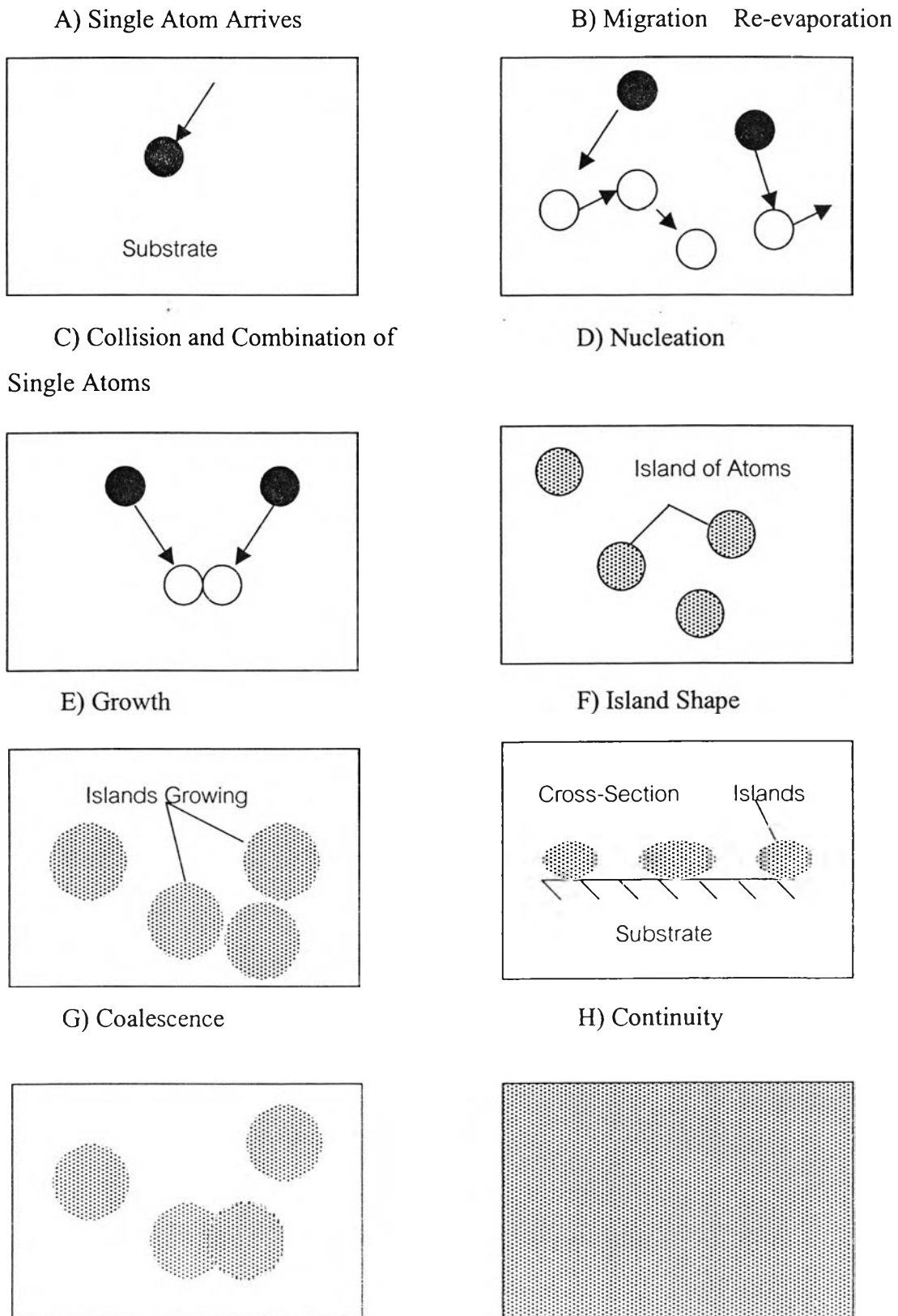
A) Single Atom Arrives

B) Migration   Re-evaporation

C) Collision and Combination of
Single Atoms

D) Nucleation

Island of Atoms

E) Growth

F) Island Shape

Islands Growing

Cross-Section   Islands

Substrate

G) Coalescence

H) Continuity

Figure 2.9: Formation of a thin film [30]

2.9 Substrate Bias Effects on Surface Mobility

In the plasma, there are many negative and positive ions. The film can be bombarded by ions, which can be controlled by applying bias at the substrate. This process leads to "bias sputtering". Generally, a negative bias voltage is applied to the substrate. So, the positive ions, which are near the substrate surface, are accelerated towards the substrate. By varying the bias voltage, the energy of the bombarding ions at the substrate can be controlled. In the process, surface mobility can be increased without an increasing of the deposition temperature.
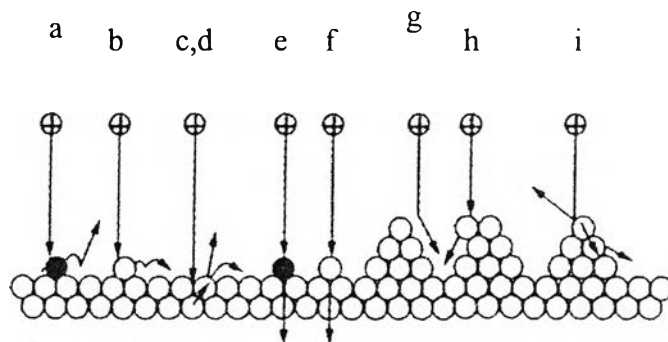

Figure 2.10: Effect of bombarding ions on the surface atoms [27]

There are many interactions on the surface from ion bombardment in low energy. The most important interactions between the ions and the surface atoms are atomic displacement, which is shown in Figure 2.10 [27]. In process a, a bombarding ion is reflected after collision and a surface atom (absorbate), which is collided by the bombarding ion receives enough energy to break the atomic bond at the surface and then it desorbs. In process b, after collision between the ion and the absorbate atom occurs, the absorbate removes on the surface. At higher energy, the removing absorbate atom can affect the surface be vacant in process c and d. In these processes, the momentum is transferred through the collision. On the other hand, if the ion has higher energy, the ion will be implanted in the film as in process e. Besides, the ion hits the surface and then the absorbate atom is implanted into the film as in process f. In process g, h and i, the ion and the sputtered atoms fill crevice film.

2.10 Key Parameters in Growth Process

The properties of film, such as morphology, hardness and crystallinity can be controlled or influenced by changing these following growth parameters.

Table2.1: The influence of the process parameters

Parameter	Effect
Magnetron Voltage	- Kinetic energy of positive ions to bombard target [30] - Maximum energy of sputtered atoms [31] - Sputtering yield (S), which is the number of sputtered atoms per bombarded ions [30] (S$\propto$ The kinetic energy of positive ions/ The surface binding energy of the target)
Magnetron current	- The number of bombarding ions per second [30] - Deposition rate of the adatoms to form a film on the substrate [29]
Total pressure, ρ	- Mean free path of the ions or the neutral atoms ($\lambda \propto \dfrac{1}{\rho}$) [24] - Density of the film relates to the mean free path. Decreasing the mean free path in the chamber due to high pressure, the density of the film decreases. At high pressure, the sputtered atoms are ejected from the target to collide the gas atoms. This phenomenon makes the sputtered atoms not have enough energy to diffuse on the substrate surface to grow the film. So, the film has microholes and pores. As a result, the film has low density [24].

Parameter	Effect
Distance between target and substrate, l	- A number of collisions that occur in space between the target and the substrate. If the distance is farther, a number of collisions in space are more. Increasing a number of collisions between the sputtered atoms and the gas atoms, the density of the film decreases [24].
Substrate temperature, T_s	- Density of film [24] High substrate temperature makes the temperature of Ar and N_2 background gas increase. This causes the density of gas and mean free path to increase. So, energy loss of sputtered atom at high substrate temperature is lower than that of at low substrate temperature. As a result, the density of the film at high substrate temperature is higher than that of at low substrate temperature. In addition, increasing the substrate temperature can make a diffusion of the adatoms increase on substrate surface. As a result, the density of the film increases. - Size of the critical cluster [29]. Increasing the substrate temperature, the size of the critical clusters increases. This phenomenon makes the size of island or grain size increase. For the film formation, the clusters containing a small number of atoms are formed by the thermodynamic fluctuation of the atoms (surface diffusion). If the size of the clusters is smaller than the critical cluster size, the clusters will be unstable and the atoms will lose from the clusters. If the size of the cluster is bigger than the critical cluster size, the clusters will be stable and have low energy. Then, the islands are formed in coalescence process. There are discontinuous islands at the high substrate temperature more than that at the low substrate temperature. Each island has one crystallographic orientation. As a result, the film may be polycrystalline at the higher substrate temperature.

Parameter	Effect
Substrate temperature, T_s	If the ratio of the substrate temperature (T_S) to film melting temperature (T_M) is less than 0.2 to 0.3, the diffusion of the adatoms on the substrate will be limited. The film will have many voids. This structural zone is called "zone 1". If T_S/T_M < 0.2-0.5, the diffusion of the adatoms will be occurred on the surface and the renucleation will be happened during the growth. The mixing between small and large grains will be occurred in this condition. In addition, the film will have fewer voids than zone1. This structural zone is called "zone T". If T_S/T_M < 0.3-0.7, the diffusion of the adatoms will be occurred on the surface and there will be the grain boundary migration in the film. This structural zone is called "zone 2". If T_S/T_M > 0.5, the diffusion of the adatoms will be occurred on the surface of the film and the bulk. Moreover, the grain boundary will migrate and the recrystallization within grains will be occurred. The film will contain large grain (sometimes columnar can be occurred). This zone is called "zone 3". Figure 2.11 shows characteristics of the 4 basic structural zones in cross section as a function of the ratio of substrate temperature to film melting temperature (T_S/T_M) and arriving ion energy (E_i).
Bias sputtering, V_s	- Hardness of the film and density of the film [23] Increasing the bias voltage, the density of films increases [23]. When the substrate is biased with a negative voltage, the positive ions in the plasma are attracted to the substrate. Then the kinetic energy of the positive ions is transferred to the surface atoms. If the energy of ions is high enough, a re-sputtering of the surface atoms will be occurred [1]. Increasing the absolute values of the negative bias, the transferred energy increases. And then, the mobility of the adatoms on the substrate surface increases. As a result, the density of film is higher. On the other hand, the electrons are attracted to the substrate and the positive ions are repelled when the substrate is biased with a positive voltage.

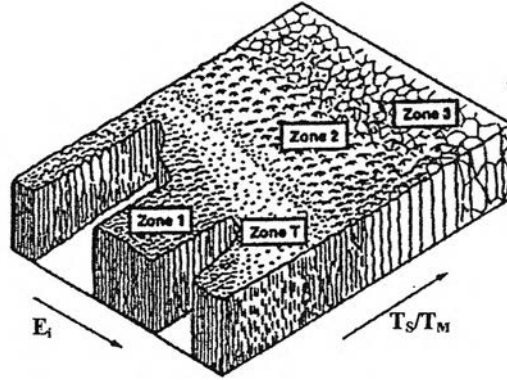| Parameter	Effect
Partial pressure of the reactive gas, ρ_p	- The stoichiometry of film [5] Increasing the partial pressure of reactive gas, the atomic fractions of reactive atoms increases almost linearly.

Figure 2.11: Characteristics of the 4 basic structural zones in cross-section [27]