CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Preparation of Intermetallic Diffusion Barriers

Plating is the general name for surface-covering techniques in which a metal is deposited onto a conductive surface. Plating is indispensable as a corrosion inhibitor for the manufacture of computers, mobile phones, and electronic devices as well as other uses such as solder ability, hardness, wear ability, friction loss, paint adhesion, conductivity, shielding, etc. Moreover, it is a key technology for the development of new machines. It is also used for decoration, for example in jewelry, typically to provide a silver or gold exterior. Thin-film deposition techniques have accomplished plating on scales as small as the width of an atom, so it is appropriate to call some plating applications nanotechnology.

There are several plating methods. For example, in one method, a solid surface is covered with a metal sheet, and then heat and pressure are applied to fuse them together (a version of this technique is called Sheffield plate). Other plating techniques include vapor deposition under vacuum, sputter deposition, and methods using vacuum conditions or gas. Recently, however, only plating techniques using a liquid tend to be called "plating". Metallizing refers to the process of coating metal on non-metallic objects.

2.1.1 Electroplating

Electroplating is the process of using electrical current to reduce metal cations in a solution and coat a conductive object with a thin layer of metal. The primary application of electroplating deposits a layer of a metal having some desired property (e.g., abrasion and wear resistance, corrosion protection, lubricity, improvement of aesthetic qualities, etc.) onto a surface lacking that property. Another application uses electroplating to build up thickness on undersized parts.

The process used in electroplating is called **electrodeposition**. It is analogous to a galvanic cell acting in reverse. The part to be plated is the cathode of the circuit. In one technique, the anode is made of the metal to be plated on the part. Both components are immersed in a solution called an "Electrolyte" containing one or more dissolved metal salts as well as other ions that permit the flow of electricity. A rectifier supplies a direct current to the cathode causing the metal ions in the electrolyte solution to lose their charge and plate out on the cathode. As the electrical current flows through the circuit, the anode slowly dissolves and replenishes the ions in the bath.

Other electroplating processes may use a non consumable anode such as lead. In these techniques, ions of the metal to be plated must be periodically replenished in the bath as they are drawn out of the solution.

2.1.1.1 Electroplating Process

The anode and cathode in the electroplating cell are connected to an external supply of direct current, a battery or, more commonly, a rectifier. The anode is connected to the positive terminal of the supply, and the cathode (article to be plated) is connected to the negative terminal. When the external power supply is switched on, the metal at the anode is oxidized from the zero valence state to form cations with a positive charge. These cations associate with the anions in the solution. The cation are reduced at the cathode to deposit in the metallic, zero valence state. Example: In an acid solution, Palladium is oxidized from an anode to Pd^{2+} by losing two electrons. The Pd^{2+} associates with the anion SO_4^{2-} in the solution to form sulfuric acid. At the cathode, the Pd^{2+} is reduced to metallic Pd by gaining two electrons. The result is the effective transfer of Pd from the anode source to a plate covering the cathode [8].

The plating is most commonly a single metallic element, not an alloy. However, some alloys can be electrodeposited, notably brass and solder.

2.1.1.2 Current density

The current density (amperage of the electroplating current divided by the surface area of the part) in this process strongly influences the deposition rate, plating adherence, and plating quality. This density can vary over the surface of a part, as outside surfaces will tend to have a higher current density than inside surfaces (e.g., holes, bores, etc.). The higher the current density, the faster the deposition rate will be, although there is a practical limit enforced by poor adhesion and plating quality when the deposition rate is too high.

While most plating cells use a continuous direct current, some employ a cycle of 8–15 seconds on followed by 1–3 seconds off. This allows high current densities to be used while still producing a quality deposit. In order to deal with the uneven plating rates that result from high current densities, the current is even sometimes reversed, causing some of the plating from the thicker sections to re-enter the solution. In effect, this allows the "valleys" to be filled without over-plating the "peaks." This is common on rough parts or when a bright finish is required.

2.1.1.3 Electroplating

A closely-related process is brush electroplating, in which localized areas or entire items are plated using a brush saturated with plating solution. The brush, typically a stainless steel body wrapped with a cloth material that both holds the plating solution and prevents direct contact with the item being plated, is connected to the positive side of a low voltage direct-current power source, and the item to be plated connected to the negative. The operator dips the brush in plating solution then applies it to the item, moving the brush continually to get an even distribution of the plating material. The brush acts as the anode, but typically does not contribute any plating material, although sometimes the brush is made from or contains the plating material in order to extend the life of the plating solution.

Brush electroplating has several advantages over tank plating, including portability, ability to plate items that for some reason can't be tank plated (one application was the plating of portions of very large decorative support columns in a building restoration), low or no masking requirements, and comparatively low plating solution volume requirements. Disadvantages compared to tank plating can include greater operator involvement (tank plating can frequently be done with minimal attention), and inability to achieve as great a plate thickness.

Electroplating is the deposition of a metallic coating onto an object by putting a negative charge onto the object and immersing it into a solution which contains a salt of the metal to be deposited. The metallic ions of the salt carry a positive charge and are attracted to the part. When they reach it, the negatively charged part provides the electrons to "reduce" the positively charged ions to metallic form.

2.1.2 Electroless deposition

Usually an electrolytic cell (consisting of two electrodes, electrolyte, and and external source of current) is used for electrodeposition. In contrast, an electroless deposition process uses only one electrode and no external source of electrical current. However, the solution for the electroless process needs to contain a reducing agent so that the electrode reaction has the form: In this work, an electroless process is used for electroless palladium plating.

2.1.2.1 Cleanliness

Cleanliness is essential to successful electroplating, since molecular layers of oil can prevent adhesion of the coating. ASTM B322 is a standard guide for cleaning metals prior to electroplating. Cleaning processes include solvent cleaning, hot alkaline detergent cleaning, electro cleaning, and acid etch. The most common industrial test for cleanliness is the waterbreak test, in which the surface is thoroughly rinsed and held vertical. Hydrophobic contaminants such as oils cause the water to bead and break up, allowing the water to drain rapidly. Perfectly clean metal surfaces are hydrophilic and will retain an unbroken sheet of water that does not bead up or drain off. ASTM F22 describes a version this test. This test does not detect hydrophilic contaminants, but the electroplating process can displace these easily since the solutions are water-based. Surfactants such as soap reduce the sensitivity of the test, so these must be thoroughly rinsed off.

Electroless plating, also known as chemical or auto-catalytic plating, is a non-galvanic type of plating method that involves several simultaneous reactions in an aqueous solution, which occur without the use of external electrical power. The reaction is accomplished when hydrogen is released by a reducing agent, normally sodium hypophosphite, and oxidized thus producing a negative charge on the surface of the part. The most common electroless plating method is electroless nickel plating. See: Electroless nickel plating

2.1.2.2 Chrome plating [9]

Chrome plating is a finishing treatment utilizing the electrolytic deposition of chromium. The most common form of chrome plating is the thin, decorative *bright chrome*, which is typically a 10-µm layer over an underlying nickel plate. When plating on Iron or Steel, an underlying plating of Copper allows the Nickel to adhere. The pores (tiny holes) in the Nickel and Chromium layers also promote corrosion resistance. Bright Chrome imparts a mirror-like finish to items such as metal furniture frames and automotive trim. Thicker deposits, up to 1000 µm, are called *hard chrome* and are used in industrial equipment to reduce friction and wear.

The traditional solution used for industrial hard chrome plating is made up of about 250 g/l of $Cr0_3$ and about 2.5 g/l of $S0_4^-$. In solution, the chrome exists as chromic acid, known as hexavalent chromium. A high current is used, in part to stabilize a thin layer of chromium

(+2) at the surface of the plated work. Acid Chrome has poor throwing power, fine details or holes are further away and receive less current resulting in poor plating. As such reasonable precautions should be taken to minimize exposure of Cr^{6+} to people and environment.

Look at the figure below, and then follow the written explanation.

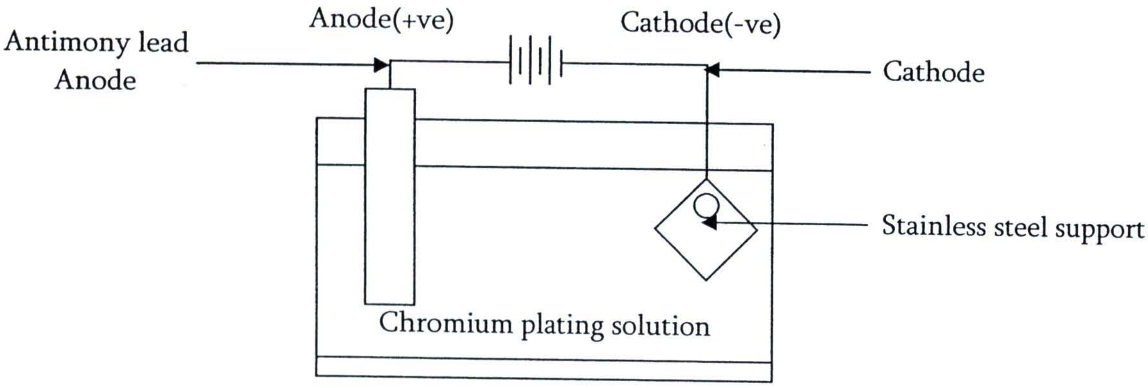

Figure 2.1 Scheme of Chromium electroplating.

Now we fill the cell with a solution of a salt of the metal to be plated. It is theoretically possible to use a molten salt, and in rare cases that is done, but most of the time the salt is simply dissolved in water and acid. The CrO_3 salt ionizes in water to Cr^{6+}

Deposition of chromium

$$Cr_2O_7^{2-} + 14H^+ + 12e^- \longrightarrow 2Cr + 2H_2O \qquad 4.1$$

Evolution of hydrogen gas

$$2H^+ + 2e^- \longrightarrow H_2 \qquad 4.2$$

Formation of chromium (III)

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O \qquad 4.3$$

At the anode, liberation of oxygen is accompanied by the oxidation of trivalent of hexavalent chromium, i.e., the regeneration of chromic acid. The reaction was exhibited in equations 4.4 to 4.6.

Evolution of oxygen gas

$$2H_2O \longrightarrow O_2 + 4H^+ + 4e^- \qquad 4.4$$

Oxidation of chromium (III) to chromium (VI)

$$2Cr^{3+} + 6H_2O \longrightarrow 2CrO_3 + 12H^+ + 6e^- \qquad 4.5$$

Formation of lead oxide

$$Pb + 2H_2O \longrightarrow PbO_2 + 4H^+ + 4e^- \qquad 4.6$$

2.1.3 Sputtering

Sputtering is a physical vapor deposition, PVD process whereby atoms in a solid target material are ejected into the gas phase due to bombardment of the material by energetic ions. It is commonly used for thin-film deposition, as well as analytical techniques

2.1.3.1 Physics sputtering

Standard physical sputtering is driven by momentum exchange between the ions and atoms in the material, due to collisions. The process can be thought of as atomic billiards, with the ion (cue ball) striking a large cluster of close-packed atoms (billiard balls). Although the first collision pushes atoms deeper into the cluster, subsequent collisions between the atoms can result in some of the atoms near the surface being ejected away from the cluster. The number of atoms ejected from the surface per incident particle is called the *sputter yield* and is an important measure of the efficiency of the sputtering process. Other things the sputter yield depends on are the energy of the incident ions, the masses of the ions and target atoms, and the surface binding energy of atoms in the solid.

The primary particles for the sputtering process are supplied either by a **plasma** that is induced in the sputtering equipment, or an ion or electron accelerator. In the plasma sputtering devices, a variety of techniques is used to modify the plasma properties, especially ion density, to achieve the optimum sputtering conditions, including usage of RF (radio frequency) alternating current, utilization of magnetic fields, and application of a bias voltage to the target.

Physical sputtering has a well-defined minimum energy threshold which is equal to or larger than the ion energy at which the maximum energy transfer of the ion to a sample atom equals the binding energy of a surface atom. This threshold typically is somewhere in the range 10–100 eV.

Preferential sputtering can occur at the start when a multicomponent target is bombarded. If the energy transfer is more efficient to one of the target components, and/or it is less strongly bound to the solid, it will sputter more efficiently than the other. If in an AB alloy the component A is sputtered preferentially, the solid will during prolonged bombardment become enriched in the B component thereby increasing the probability that B is sputtered such that the composition will approach AB again.

2.1.3.2 Film deposition

Sputter deposition is a method of depositing thin films by **sputtering**, i.e. eroding, material from a “target,” e.g., SiO_2, which then deposits onto a "substrate," e.g., a silicon wafer. Resputtering, in contrast, involves re-emission of the depositedd material, e.g., SiO_2, during the deposition also by ion bombardment.

Sputtered atoms ejected into the gas phase are not in their thermodynamic equilibrium state, and tend to deposit on all surfaces in the vacuum chamber. A substrate (such as a wafer) placed in the chamber will be coated with a thin film. Sputtering usually uses argon plasma.

2.1.3.3 Fundamental processes in plasma

Inside plasma, there are electrons, ion of various charge state, neutral atoms and molecules. These particles move around inside the plasma with kinetic energy. The particles may exchange energy when they collide with each other. This collision can be either elastic or inelastic.

For elastic collision, the energy is conserved and the particles only exchange kinetic energy. The magnitude and directions of the velocities of both particles changes after the collision. However, during an inelastic collision, the internal energy of the colliding particles can be changed as well. This leads to various types of processes such as excitation and ionization other than just scattering found in elastic collision.

For a general knowledge of basic mechanics, the fraction of energy transferred during an elastic collision is:

$$\delta = \frac{kinetic \quad of \quad m_2 \quad after \quad collision}{initial \quad kinetic \quad energy \quad of \quad m_1} = \frac{4m_1m_2}{(m_1+m_2)^2}\cos^2\theta$$

where θ is the angle that m_1 made with m_2 after collision occur. This shows the energy of electron can be transferred to the internal energy of m_2 which may be ion or atom under inelastic scattering process.

As a consequence of collisions among the particles in the plasma, four elementary processes may occur. These are described as follow.

- **Scattering**

$$A + e \longrightarrow e + A \qquad 4.7$$

This is the process caused by elastic collision where the colliding electron will transferred a small fraction of its kinetic energy to the atom or ion.

- **Excitation**

$$e + A \longrightarrow A^* + e \qquad 4.8$$

This process occurs when electron with sufficient energy colliding inelastically with an atom or ion and part of its energy is absorbed by an inner shell electron of the atom or ion. This inner shell electron is raised to a higher energy level where the atom or ion is now deemed to be is an excited state.

Most of the excited states have a short life time. The excited electron will decay back to its original level. In doing so, it emits a photo which is equivalent to the energy difference. This process is called de-excitation or relaxation by spontaneous emission.

- **Ionization**

$$e^- + A \longrightarrow A^+ + 2e^- \qquad 4.9$$

With sufficiently high energy, the colliding electron may transfer enough energy to the target atom or ion to release a bound electron from its level. The atom or ion loses an electron and it is said to be ionized. They will become one charge state higher.

- **Recombination**

$$e^- + A^+ \longrightarrow A + (h\nu) \qquad 4.10$$

Recombination process occurs when electron collides with ion and the electron is captured and occupies the vacancy inside the ion. The charge state if the ion is changed to one level lower than previously. Excess energy of electron is released in a form of photon emitted with energy *hv*

By deriving an impact parameter of a collision between atom and electron(in general physics) such that:

$$b_o = \frac{Z_1 Z_2 e^2}{4\pi\varepsilon_o (3KT)}. \qquad 4.11$$

2.1.3.4 The concept of Glow discharge

The sputter deposition process is that the target material, which is bombarded by energetic ions, releases atoms. After gas phase transport through the process chamber, these atoms then condense on the substrate to from a film a film, as shown schematically in Fig. 2.2

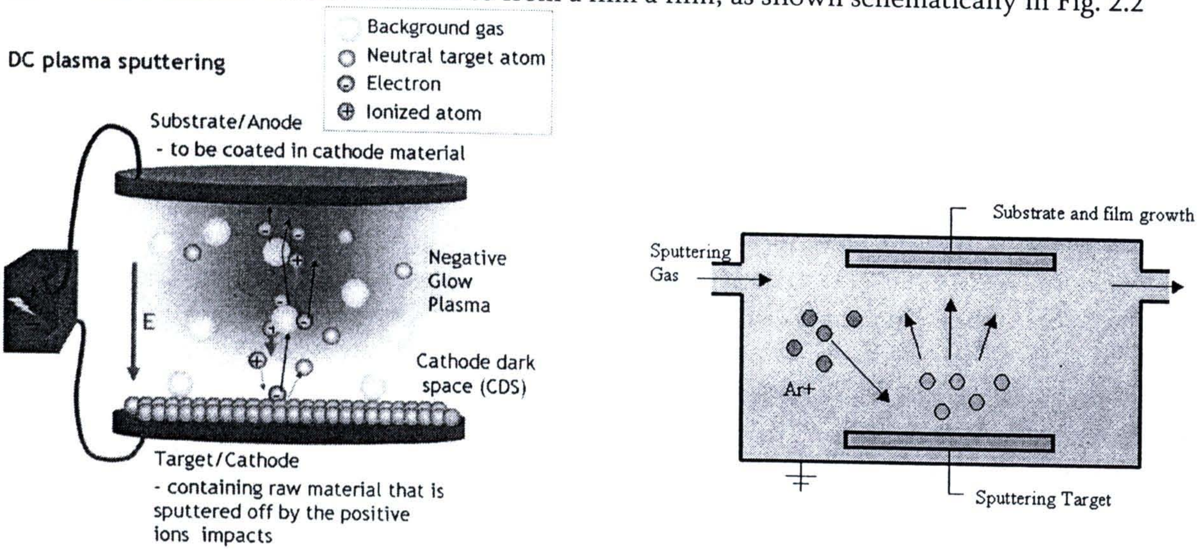

Figure 2.2 Schematic of a basic DC sputtering deposition system.

After a sputtering gas has been introduced into a vacuum chamber, a negative potential is applied to the target. This induces a glow discharge process in the deposition chamber. The ions are accelerated toward the target by the applied potential.

In the collisions between ions and target material, energy and momentum of the incident ions are transferred to the target. If the energy of the target atoms becomes high enough to overcome the surface binding energy, it will cause the atoms of the target to be *sputtered* away and travel to the substrate. This energetic ion bombardment of the target will also cause the generation of secondary electrons that are accelerated away from the target due to the electric field. As we follow the secondary electrons that come out from the target (cathode), they first cross "the dark space," sometime known as the "sheath region" It is name "dark space" because the electron density is very low, reducing excitation of gas atoms in this area, thus reducing glow from their excited states. Due to reduced ionization in the dark-space, most of the applied target potential is dropped over the dark space. The thickness of this dark space depends upon the sputtering pressure and equals the mean free path of the secondary electrons from the cathode. Strong fields, therefore, are formed. Since the secondary electron follows the electric field, which is perpendicular to the cathode surface, they travel in the broad parallel beam and are known as "beam" electrons. After acceleration, they pass into "the negative-glow" region, where they ionize gas molecules and lose their directionally by scattering. In this way, these secondary electrons will sustain the glow discharge process.

2.1.3.5 Thin film synthesis by sputtering

Intermetallic diffusion barriers were grown by using reactive magnetron sputter deposition. Sputtering can be very well controlled and is generally applicable for metals, semiconductors as well as insulators. Furthermore, it gives more degree of freedom to control growth parameters, such as, substrate temperature and kinetic energy of species arriving to the surface of the substrate, than other thin film deposition process. This gives a lot of benefits for many thin film application, such as the growth of alloys and the use of ion-surface interaction for microstructure modification

2.1.3.6 Reactive sputtering

Normally, the sputter deposition of pure metal can be done by using an inert gas, such as argon (Ar). For a compound thin film, as in this work; CrN, chemical reaction between the target material and the sputtering gas are required to be able to form such a film. This process in sputtering is called *reactive sputter deposition* [10] and is commonly used. Generally, a mixture between an inert gas and a reactive gas, such as N_2, O_2 and CH_4, can be used in the process. This gives the possibility to alter compound stoichiometry in sputtering from a compound target or to deposit a compound film from a metallic target. A typical behavior of reactive sputtering upon increasing the content of reactive gas in the gas mixture is the increasing compound coverage of the active target surface. The compound material on the surface is then sputtered away from the surface instead of the pure metal. This will change the deposition process and require an optimization of the process parameters since the compound usually have low sputtering rate. In the CrN thin film synthesis in this work, nitrogen gas with very high purity (99.999999999%) has been used as sputter gas, with reacts with the aluminum target and forms a compound CrN layer on the target surface. The sputtering of this compound layer then creates a 1:1 flux of the Cr and N towards the substrate

2.2 Diffusion

2.2.1 Introduction of diffusion

Simply put, diffusion is the phenomenon of material transport by atomic motion. This unit discusses the atomic methods by which diffusion occurs, the maths behind it, and the influence of temperature and materials used, on the rate of diffusion. This unit will introduce the topic of diffusion, how it occurs, and some examples of its use in industry.
If two pieces of different metal are joined together as shown here in figure2.3 for example, palladium and stainless steel alloy, and they are then heated for a long time (but below their melting points), the atoms from the metals migrate, or diffuse into the other.

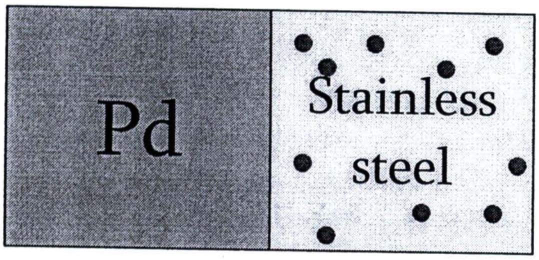

Figure 2.3 Diffusion between two pieces of difference metal.

Concentrations of both metals vary with position. This process is known as *interdiffusion*, and is a time dependent process.

2.2.2 Mechanisms of diffusion

At an atomic level, atoms are arranged in a lattice pattern, e.g. as shown simply in the diagram. Diffusion is just the stepwise migration of atoms from lattice site to lattice site. One type of diffusion involves the exchange of an atom from its normal lattice position, to an adjacent vacant lattice site or vacancy. This is known as substitutional or vacancy diffusion. Of course, this process requires the presence of vacancies, and vacancy diffusion depends on the extent of vacancies in the material. The second type of diffusion involves atoms that migrate from an "interstitial" or "in-between" position, to a neighboring one that is empty. This occurs with the infusion of impurities such as Hydrogen or Carbon, which have atoms that are small enough to fit into the interstitial positions. This process is called, as you might expect, interstitial diffusion. The mechanisms of diffusion have 3 types as shown in Figure 2.4.

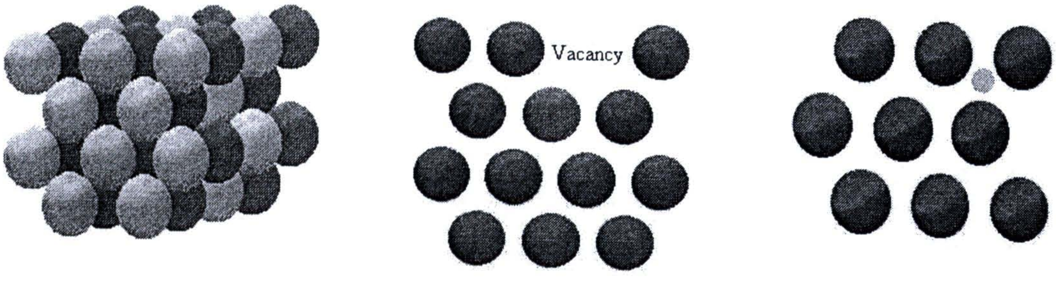

Figure 2.4 Three types of diffusion phenomena.

Steady-State Diffusion

Diffusion is a time-dependent process, and often it is necessary to know how fast it occurs, or the rate of mass transfer. This rate is known as the *diffusion flux*, J, and is defined as the mass, M, diffusing through a unit cross-sectional area of solid, per unit of time. Therefore,

$$J = \frac{M}{AT} \qquad 4.12$$

where A is the area across which diffusion is occurring, and T is the elapsed diffusion time. If the diffusion flux does not change with time, a steady state condition exists, and this is called *steady-state diffusion.*

Non-Steady State Diffusion

In real life, most diffusion is non-steady state, i.e. the diffusion "flux", J, varies with time. Look back at the graph showing the concentration gradients between palladium and Stainless steel alloy. It is how "harsh" this concentration gradient is, that determines this flux, which is how quickly diffusion is occurring. The concentration gradient drives diffusion: a high gradient means a high flux.

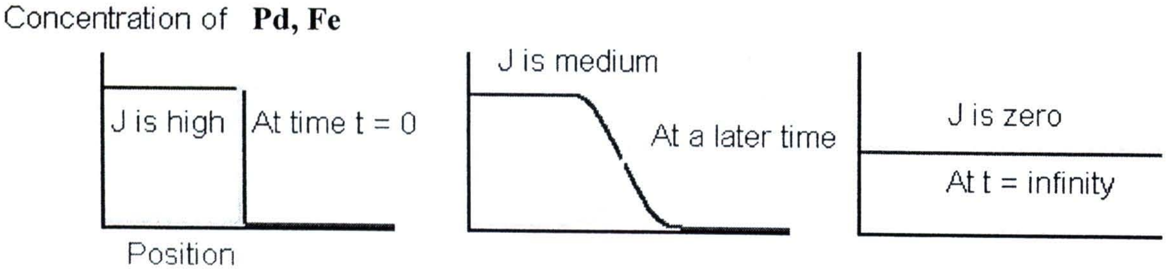

Figure 2.5 Diffusion flux between Pd and metal atoms in SS occurring non-steady state.

This means that the last equation we used is no longer valid. In these situations an equation known as Fick's First Law is used:

States that the rate of diffusion, or flux, J of a species is proportional to the concentration gradient, ∂C/∂x:

$$J = -D\frac{\partial C}{\partial X} \qquad 4.13$$

where D is the diffusivity or *coefficient of diffusion*. For atomic diffusion the units are:

J	atoms m-2s-1
D	m2s-1
∂C/∂x:	atoms m-4.

And the Fick's second Law is used:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \qquad 4.14$$

where C is the concentration of the substance you're looking at (measured between 0 and 1). D is known as the diffusion coefficient, and is given in square metre per second.

In real life some simple boundary conditions can be applied to materials. These are that:

- x is the distance from the interface you're looking at, and=0 at the surface or interface of the material.
- The instant before diffusion starts, time is taken as zero, and
- Before diffusion starts, all the atoms that will be diffusing are evenly distributed. Because of these boundary conditions.

2.2.3 Factors that influence diffusion

2.2.3.1 Diffusing species

The magnitude of the diffusion coefficient, D, is a measure of the rate at which atoms diffuse. The diffusing species, as well as the host material, influences the diffusion coefficient. For example, if a diffusing species has smaller atoms, it will interstitially diffuse through a host material more easily. Also substitution of diffusion is made easier if the host material has lots of vacancies to start with.

2.2.3.2 Temperature

Temperature has the most profound influence on the coefficients and diffusion rates. For example, for the self-diffusion of Fe in alpha Fe, the diffusion coefficient increases about five times, after the temperature is raised from 500 to 900°C. This is because diffusion is a thermally activated process-i.e. there is an energy barrier (activation energy) that has to be overcome, in order for the atoms to move from one lattice site to the other.

The more thermal energy there is around, the easier it is for this energy barrier to be overcome. Therefore, there is an exponential relationship between Temperature (T), and Diffusion Coefficient (D), and this is:

$$D = A \cdot e^{-\frac{Q}{RT}} \qquad 4.14$$

where Q = activation energy, T = temperature in Kelvin, R = Universal Gas Constant, and A is a constant. Taking natural logarithms of this equation,

$$\ln D = \ln A^{-\frac{Q}{RT}}. \qquad 4.15$$

And since A, Q and R are all constants, this expression is similar to the equation of a straight line: $y = mx + C$.

X-ray Photoelectron spectroscopy, XPS technique

X-ray photoelectron spectroscopy is a surface sensitive spectroscopy technique that allows chemical identification of the elements in the top atomic layers of a sample by recording the binding energies of the electrons associated with these atoms. Furthermore, because the binding energies differ not only from chemical species to species, but also vary with the bonding conditions in which the element is found, this technique also provides information on the actual compounds present on the surface. In essence, it probes the electronic structure of the surface. When used in combination with sputter depth profiling, in which ions are used to remove surface layers from a sample, XPS provides information about the binding energy spectra of a sample.

The information provided by XPS is complementary to the data obtained with other techniques, as it provides information about the true electronic structure of the surface. Binding energies are sensitive to local environments of atoms or ions in materials, information about which is not accessible through regular (EDS or WDS) spectroscopy techniques.

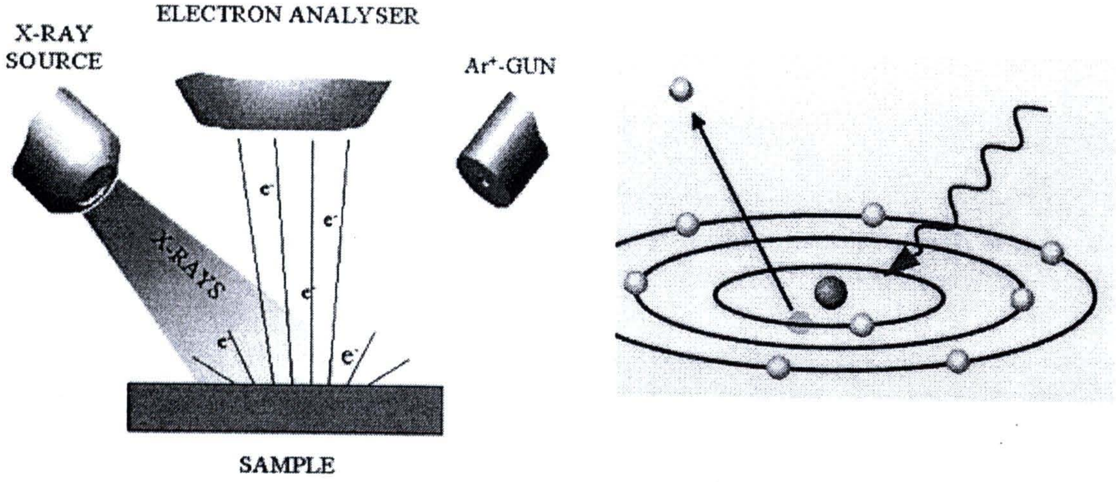

Figure 2.6 Concept of XPS technique.

X-ray photoelectron spectroscopy (XPS), also known as Electron Spectroscopy for Chemical Analysis (ESCA), is a widely used technique for obtaining chemical information of various material surfaces. Core-level electrons are emitted from a surface after it has been irradiated with soft X-ray. The low kinetic energy (0-1500 eV) of emitted photoelectrons limit the depth from which it can emerge so that XPS is a very surface-sensitive technique and the sample depth is in the range of few nanometers. Photoelectrons are collected and analyzed by the instrument to produce a spectrum of emission intensity verse electron binding energy. In general, the binding energies of the photoelectrons are characteristic of the element from which they are emanated so that the spectra can be used for surface elemental analysis. Small shifts in the elemental binding energies provide information about the chemical state of the elements on the surface. Therefore, the high resolution XPS studies can provide the chemical state information of the surface [11].

2.4 Literature reviews

Wang *et al.* [12] reported that metallic particles embedded in the oxide film play an important role in film's optical property. The result showed that metallic phases of Ag, Ti, and Pb can be formed in different oxide films under heating, X-ray photon, and electron radiation. The metallic phase separated from metal oxide film was investigated by X-ray photoelectron spectroscopy technique. Metal oxygen bond breaking and total energy reduction in the film. It is necessary to fully understand the formation mechanism of metallic particles so their shapes and distributions can be tailored to achieve the desired film's properties. Thermal activated metallic phase formation in first two cases can be explained by the bond breaking and reduction of total energy.

Shen *et al.* [13] reported that nanocrystalline chromium nitride (CrN) with the cubic rock-salt structure was synthesized by the arc discharge method in nitrogen gas (N_2). The product was characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). It was found that the nitrogen gas pressure is a crucial factor for the synthesis of cubic CrN. At relatively low N_2 pressure, cubic CrN was formed. With the increase of N_2 pressure, hexagonal Cr_2N and metal Cr were gradually formed. It indicated that the formation of CrN is enhanced at a low nitrogen pressure environment, and the diffusion of nitrogen atoms into the Cr was lowered with the increase of N_2 pressure. They explain this experimental observation in terms of the evaporation rate of anode Cr and the ionization of nitrogen. In conclusion, they have synthesized the cubic CrN nanocrystalline at a low nitrogen pressure of 5 kPa by the DC arc discharge method. The sizes of most CrN particles are less than 10 nm, with the increase of the nitrogen pressure, the amount of CrN decreases and the amount of Cr_2N and Cr increases. This indicates that the ability of nitridation falls, and the particle size also becomes much larger. The low-pressure synthesis of cubic CrN should be beneficial to improve nitridation of other transition metals such as, Co, Ta, Mo, and W.

Yan and Roland [14] reported that the integrity of thin composite palladium membranes is influenced by the surface roughness of the porous support. Supports with smooth surface and small pore size are expensive as they are composed of several layers with decreasing pore size which require multiple successive energy and time consuming sintering steps. In addition, smooth surfaces may cause poor membrane adhesion. It is therefore of interest to develop methods for preparation of thin defect-free palladium membranes over supports with rough surfaces. Atmospheric plasma spraying produced relatively thick continuous films, but with some residual open porosity. Electroless plating gave the densest layers. Activation of the support surface by metal organic chemical vapor deposition of palladium instead of the conventional sensitization and activation pretreatment based on successive immersion in $SnCl_2$ and $PdCl_2$ solutions allowed to reduce the membrane thickness without compromising its integrity.

Arias *et al.* [15] reported that thin films of TiN and ZrN were grown on stainless steel 316 substrate using the pulsed cathodic arc technique with different number of discharges (one to five discharges). The coatings were characterized in terms of crystalline structure, microstructure, elementary chemical composition and stoichiometric by X-ray diffraction (XRD), atomic force microscopy (AFM) and X -ray photoelectron spectroscopy for chemical analyses (XPS), respectively. The XRD results show that for both TiN and ZrN, the preferential direction occurs in the plane (2 0 0), and this observation remained- even when the number of discharges was increased. The grain size is increased with the increase of the number of discharges for both nitrides, the roughness for the TiN film is greater than for the ZrN film. XPS analysis determined that there is a higher nitrogen presence in the ZrN film than in the TiN film.

Stefanov *et al.* [16] reported that the structure and composition of chromium oxide films formed on stainless steel by immersion in a chromium electrolyte have been studied by SEM and XPS. Cr_2O_3 crystallites in the range 30–150 nm are fully developed and cover the whole surface. The chemical compositions in the depth and the thickness of the oxide layer have been determined by XPS sputter profiles. The oxide film can be described within the framework of a double layer consisting of a thin outer hydrated layer and an inner layer of Cr_2O_3.

Lacoste *et al.* [17] reported that implantation of oxygen in stainless steel (15% Cr) via plasma-based ion implantation in a distributed ECR plasma reactor has been studied as functions of ion energy and dose. Due to the formation at the surface of dielectric films with optical index and thickness depending on the implantation time and pulse voltage (up to 44 kV), various colorations can be obtained. The experimental results demonstrate the feasibility of uniform processing, the possibility of reaching perfect control of the coloring through the dose and energy of implanted ions, and that the resulting coloration varies monotonically when increasing the dose and penetration depth of implanted oxygen. Characterization of the films by scanning electron microscopy and X-ray microanalysis shows that oxygen implantation results in strong surface oxidation, but without any significant degradation of the surface aspect. The thickness and composition profiles of the oxide layers determined using X-ray photoelectron spectroscopy, increases with ion energy and dose, but that the composition of the oxide layer resulting from. A uniform iron oxide layer (with a stoichiometry closed to Fe_2O_3), free from chromium, is formed in the near-surface region, while chromium segregates at the interface between the oxide layer and the bulk stainless steel to form chromium oxide Cr_2O_3.

Huiyuan *et al.* [18] reported that thin Pd–Cu membranes were prepared by electroless plating technique on porous stainless steel (PSS) disks coated with a mesoporous palladium impregnated zirconia intermediate layer. This intermediate layer provided seeds for electroless plating growth of Pd–Cu film during synthesis and serves as an inter-metallic diffusion barrier that improved membrane stability for practical application. XPS analyses showed that the average surface compositions of the two membranes were respectively $Pd_{84}Cu_{16}$ and $Pd_{46}Cu_{54}$ (at.%).

Sabioni *et al.* [19] prepared chromium protective layers were formed on many industrial alloys to prevent corrosion by oxidation. The role of such layers was to limit the inward diffusion of oxygen and the outward diffusion of cations. A number of chromium forming alloys contain iron as a major component, such as the stainless steels. To check if chromium is a barrier to the outward diffusion of iron in these alloys, iron diffusion in chromium was studied in both polycrystals and oxide films formed by oxidation of Ni–30Cr alloy in the temperature range 700–1100 .C at an oxygen pressure equal to 10.4 atm. An iron film of about 80 nm thick was deposited on the chromium surface, and after the diffusing treatment, iron depth profiles were established by secondary ion mass spectrometry (SIMS).

Two diffusion domains appear whatever the nature of the chromium material, polycrystals or films. In the first domain, using a solution of the Fick's second law for diffusion from a thick film, effective or bulk diffusion coefficients were determined.

Sato *et al.* [6] investigated the oxidation behaviors of modified SUS316 (PNC316) and SUS316 stainless steels under the low oxygen partial pressure of 10^{-31}- 10^{-22} atm at 600–800°C. Oxygen uptake by these materials parabolically increased with time, and the kinetic rate constants depended on both oxygen partial pressure and temperature. For the duplex layer formed under the low oxygen partial pressure, the inner layer consisted of such oxides as Cr_2O_3 and $FeCr_2O_4$, while the outer layer consisted of non-oxidized a-Fe. Furthermore, oxidation along the grain boundaries was observed for samples oxidized for a longtime. From the point of view of fuel cladding chemical interaction evaluation at high burn-up fuel for fast reactors, it is interesting that formation of non oxidized a-Fe was observed under the low oxygen partial pressure.

Huntz *et al.* [20] reported that the oxidation behaviour of AISI 304 and AISI 439 stainless steels was studied at high temperatures, under various oxygen pressures and in the presence or not of water vapor. Thermogravimetric analyses were conducted in isothermal conditions from 850 to 950°C for 50 h and micro structural and chemical analyses of the oxide films grown by oxidation were performed by SEM and EDX. The oxide films were also analyzed by grazing X-ray diffraction and by X photoelectron spectroscopy (XPS). The AISI 439 steel has higher oxidation resistance than AISI 304, above 850°C, under high oxygen pressures. On the other hand, the AISI 304 steel has higher oxidation resistance under low oxygen pressures in the whole temperature range. In order to check whether the growth kinetics of Cr_2O_3 formed by the oxidation of stainless steels was controlled by oxygen or/and chromium diffusion through the oxide film.

Earl *et al.* [21] studied the rates of oxidation of three heater alloys of nominal composition 80% nickel-20% chromium were studied over the temperature range of 500° to 950°C and at a pressure of 7.6 cm of Hg of oxygen, using the vacuum microbalance method. Temper color films were obtained for all oxidations below 850°C, while gray or gray-green films were obtained at temperatures of 850°C and higher. No evidence was found for scaling or cracking of the oxide from the alloys on cooling at temperatures of oxidation up to 950°C.The parabolic rate law was applied to the data. Reasonable agreement was found for temperatures above 650°C, while below this temperature the parabolic rate law constant varied with time. This time variation was explained in terms of composition changes in the oxide and growth of the oxide crystallite size. The classical theory of diffusion was used to interpret effect of temperature on rate of oxidation, and heats, entropies, and free energies of activation for the overall reaction were evaluated from the data.