Chapter Two

2.0 Theoretical background

2.1 The History of thin-films

In 1873, the work of Clerk Maxwell, A treatise on electricity and Magnetism, was published, the system of equations and the basic theory for the analysis of thin film optical problems.

In1886, Lord Raleigh reported to the royal society an experimental verification of Fresnel,s reflection law at near normal incidence and he found it necessary to use freshly polished glass because the reflectance of older material, even without any visible signs of tarnish, was too low .

In 1932s, Rouard observed that a very thin metallic film reduced the internal reflectance of glass plate. Then, in 1939, Geffcken, s work describes the improved antireflection coating and his creation of the famous quarter-half-quarter design. In 1989s, Courtaulds Performance Films founded. (CPF films) Modern erna, further discussion will focus on thermal evaporation optical Thin Film deposition technology.

Thin films are just thin layers of material, usually less than 1μm thickness and sometimes as thin as 1nm. In the optical field, films with thickness less than the wave-length of light (~1o7m) are used to make transmitting and reflecting devices based on interference principles. A thin film is more, presented with a piece of unknown bulk material for identification of surface [16].

2.2 The production of thin film

There is considerable number of processes that can be used for the deposition of optical coatings. The comments take place under vacuum and can be classified as physical vapor deposition witch abbreviated to (PVD) and chemical vapor deposition (CVD).

2.3Thin film deposition techniques

Thin film technology, like crystal growth is one of the oldest arts and one of the newest sciences’. The ancient craft of gold peating has-been practiced for at least four thousand years. Today, gold leaf can be machine beaten to 0.05micron. By now films of all kinds of materials, running to several thousand, have been prepared by arrange of techniques. Thin materials may also be formed from a liquid or a paste, in which case it is called a thick film. Its microstructure and properties depending on how the atoms-molecules-ions cluster of species are created for the condensation process, the methods for depending thin films termed physical vapor deposition (PVD), chemical vapor deposition (CVD),electrochemical deposition or mixture of (PVD)and (CVD)[17].

2.3.1 Physical Vapor Deposition:

In physical vapor deposition processes, the thin film condenses directly in the solid phase from vapor, and formed by atoms directly transported the form source to the substrate through gas phase with specific conditions. Physical Vapor Deposition methods are simplicity, flexibility and relatively low cost.

2.3.2 Evaporation:

Evaporation methods are perhaps the simple’s means of producing thin films and coating comprising of sequentially deposited atoms of evaporation techniques. Thin film depositions have been superseded in many instances by sputtering and chemical vapor deposition methods largely due to difficulties in achieving conformal converge. In the past few decades, advances in our understanding of physics and chemistry of ionized gases have led to the widespread adoption of plasma technology for thin film deposition and removal microelectronics application has been the main technological driver in this regard. Historically, the challenges in microelectronics, virtually single handedly thrust enormous scientific interest in the physics and chemistry of plasma and glow discharges in to the main arena of thin film technology.

In most cases the only film dimension considered has been the thickness, a variable controlled by the growth or deposition processes. However fabrication of thin film devices for all sorts of application, not only microelectronics. Generally requires that they be geometrically defined laterally or patterned in the thin film plane. Century ago CVP methods were used to deposit a protective tungsten coating on carbon filaments in an attempt to exempt to extend the life incandescent lamps.

Today high temperature CVD processes for producing thin films and coating have found increasing application in such diverse technologies as the fabrication of ball bearing and cutting tools , the production of rocket engines and nuclear reactor components . In thin film technology research's interested in deposition of thin film and thin film structure [17.18].

2.3.4 Thermal evaporation:

In thermal evaporation the vapor is simply by heating the material, evaporation is one of the most famous two physical methods of preparation of thin films; evaporation is more widely known and used. A vast number of material can evaporated in vacuum and be caused condense on surfaces. Most of these materials can be sublimed, for example magnesium, cadmium, Zinc sulfide…etc.

In evaporation processes describe evaporation rate (flux) from kinetic theory for evaporation, the vapor pressure is:

$$P_{evaporation} = 3x10^{12}\sigma^{\frac{3}{2}}T^{-\frac{1}{2}}e^{\left(\frac{\Delta H}{nKT}\right)} \approx P_o^{\left(\frac{E\alpha}{KT}\right)} \qquad (2.1)$$

Where σ is the surface tension of the liquid,

n is Avogadro’s number

T is absolute temperature

and ΔH is the enthalpy of evaporation (the energy required to convent from a liquid to gas phase).

To define the number of molecules crossing a plane per unit time as:

$$J = \sqrt{\frac{p^2}{2\pi KTm}} \qquad (2.2)$$

Where P is pressure in Pascal’s,

K is Boltezmann constant,

T is absolute temperature

and m is the atomic or molecular mass.

If the liquid is assumed to be a constant temperature and the deposition rate is:

$$R_d = \sqrt{\frac{p^2}{2\pi KTm}} \cdot \frac{P_{evaporation}}{\sqrt{T}} \cdot \frac{Area}{4\pi r^2} \qquad (2.3)$$

Where p is the mass density (kg/m2).

Area is the area of the wafer.

And r is the radius of the sphere.

2.3.5 Electron-beam evaporation (e-beam):

Electron beam evaporation sources are employed in the production of a multitude of low and hi tech products including: sunglasses, camera lenses, optical filters, infrared detectors, superconductors, automotive decorative trim, costume jewelry, corrosion resistant surfaces and many others.

Disadvantages of resistivity heated evaporation sources include contamination by crucibles, heaters and support materials and the limitation of relatively low input power levels. This makes it difficult to deposit pure films or evaporate high –melting –point materials at appreciable rates.

2.3.6 Laser deposition of thin films:

The word "laser" is an acronym for Light Amplification by Stimulated Emission of Radiation. Lasers are finding ever increasing military applications -principally for target acquisition, fire control, and training. These lasers are termed rangefinders, target designators, and direct-fire simulators. Lasers are also being used in communications.

The Helium-Neon laser was the first continuous laser. It was invented by Javan et. al. In 1961, Nowadays lasers are usually pre-adjusted using a He-Ne laser. But how did Javan manage to do this,this shows that it is no coincidence that Javan's first He-Ne laser oscillated at a wavelength of 1.5µm, since the amplification at this wavelength is considerably higher than the 632 nm line which is reached at what is now commonly known as the red line, which was made to oscillate only one year later by White and Ridgen.

The similarity between the manufacturing techniques of He-Ne lasers and electron valves helped in the mass production and distribution of He-Ne lasers.

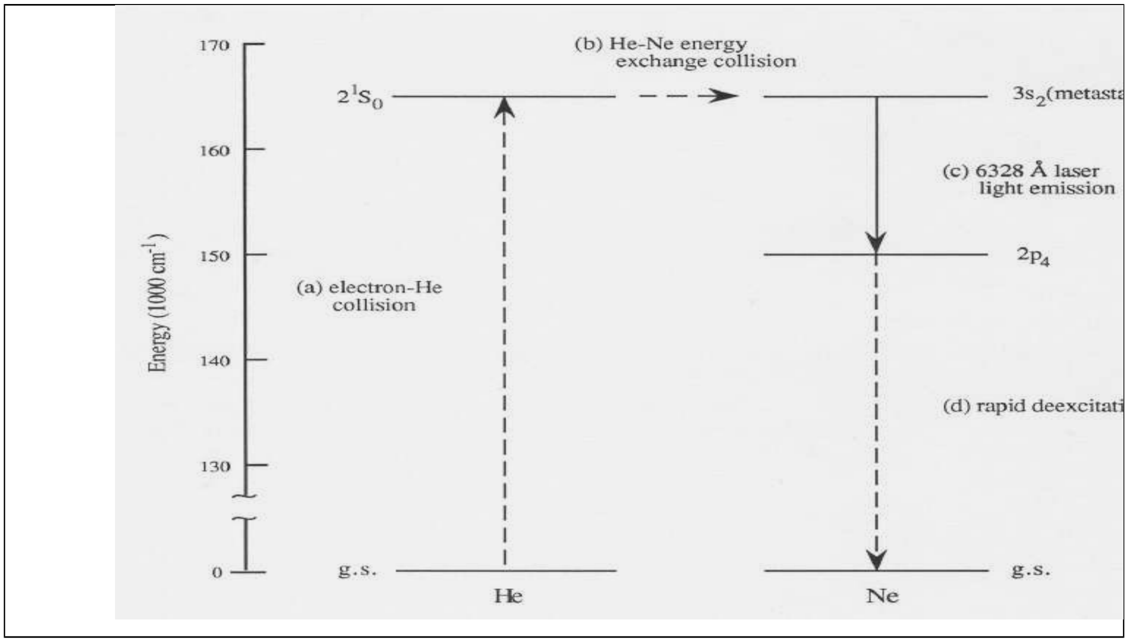

Figure 2.1 Simplified atomic energy level diagram showing excited states of atomic He-Ne that are relevant to the operation of the He-Ne laser at 632nm.

Laser vaporization has been utilized for deposition of thin films for very applications. In a typical deposition experiment, the laser beam, usually form a pulsed laser with high peak power, is directed at target of the material to be deposited. The process is usually carried out in vacuum, or at least a partial vacuum. The laser evaporates material from the target surface. The substrate to be coated is coated a short distance from the target. Some of the evaporated material condenses on the substrate. This leads to growth of a thin film of the desired material. In some cases, the composition of the film may be varied by chemical interactions with ambient gas in the system.

There have been many demonstrations of the growth of a wide variety of thin films, including metals, insulators, and semiconductors. But the transition to use of laser deposition for production has been slow. There has been substantial interest in the use of laser for deposition of high – temperature superconducting thin films, and potential utility of laser ablation for deposition of superconducting films [19].

2.3.7 Chemical Vapor Deposition:

Film is formed by chemical reaction on the surface of substrate. It differs from physical vapor deposition (PVD), in that the film material is produced by a reaction amongst components of the vapor that surrounds the substrates, which relies on material transfer from condensed phase evaporator or sputter target sources.

Thin films of MnS also deposit on glass substrates by the chemical bath deposition method, for example (manganese chloride with ammonium sulfide) can be prepared by reacting a manganese salt, which are precipitated out of the solution and deposited as thin films. Reaction equations of MnS film deposition are as shown below [20, 21].

$$(NH_4)_2S + MnCl_2 \longrightarrow 2\ NH_4Cl + MnS \qquad (2.4)$$

Spectrophotometric analyses of the films were carried out for the optical properties: absorbance, transmittance, reflectance, refractive index, and absorption coefficient. The optical properties of the films within the UV-NIR indicate that the films can find application in solar thermal technology, particularly in antireflection coating [22].

2.3.8 Sputtering:

Sputtering is a technology in which the material is related from the source at much lower temperature than evaporation. The substrate is placed in a vacuum chamber with the source material, named a target, and an inert gas (such argon) is introduced at low pressure, the type source in these technology including DC sputtering and magnetron sputtering [23].

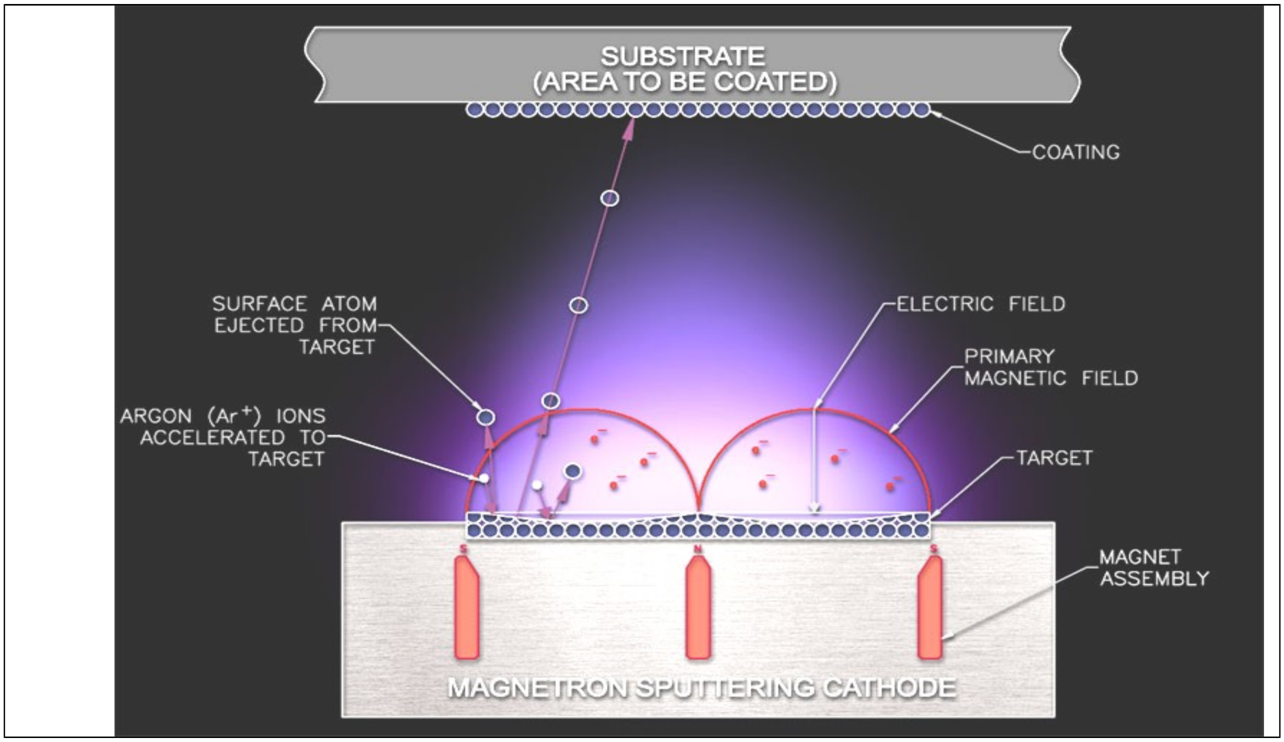

Figure 2.2Magnetron sputtering process.

2.3.9 Coating:

In this process the material to be deposited is dissolved in liquid from in a solvent. The material can be applied to the substrate by spraying or spinning. Once the solvent is evaporated, a thin film of the material remains on the substrate. This is particularly useful for polymer materials, which may be easily dissolved in organic solvent, and it is the common method used to apply photo resist to substrates (in photolithography). The thicknesses that can be cast on a substrate range all the way from a single monolayer of molecules (adhesion promotion) to tens of micrometers. In recent years, the casting technology has also been applied to form films of glass materials on substrate [24].

2.3.10 Spin coating:

Spin coating is a producing used to apply uniform thin film to flat substrates. In short, an excesses amount of the solvent is placed on the substrate, which is then rotated in high speed in order to spread the fluid by centrifugal force. The thickness of thin film also depends on the concentration of the solution and the solvent.

Advice used for spin coating is called a spin coater which is very popular in microlithography and the semiconductor industry. In principle, they consist of a high speed motor with a vacuum plate attached on the top. Spin coating can used to create thin films with thicknesses in nano scales. There are two main applications for these processes [25, 26].

The production of ultra thin photo resist films (with thickness less than 200nm) necessary for the manufacturing of microelectronic devices, the deposition of magnetic dispersion on aluminum substrate during the production of magnetic memory devices.

The spin coating process can be divided into three major stages, A. deposition, B.spin up, and D. evaporation of solvent.

2.4 Antireflection:

Antireflection coating consist of one or more thin layers film of material, each layer having a specific thickness and a specific refractive index. Transitions from one layer to another represents an index of refraction discontinuity. Thus as a beam of light travels through the layers, it is partially reflected by the refractive index discontinuities.

These reflections, on their way back interfere destructively, canceling each other out, and thus no reflection emerges from the layers. For example, to minimize the reflected optical power of incident light on glass, the layer that interfaces glass with air has a low refractive index. In an arrangement of a single antireflection thin film, two requirements must be satisfied:

$$n_2 d_2 = \frac{m\lambda}{4} \qquad (25)$$

$$n_2 = \sqrt{(n_1 \cdot n_3)} \qquad (2.6)$$

Where x2 is the film thickness

and m is an odd integer (1, 3, 5…)

In practice, it is very difficult to find materials with a refractive index n2, as calculated by the last relationship, if n1 is for air = (1) and n3 is for standard glass = (1.52), then n2 is calculated to be (1.23).

2.5 Transmission and reflection of coating on substrate:

Many multilayer coating are deposited on to transparent or partially transparent substrate. Both the multilayer and the substrate contribute to the overall performance of the filter. For example, absorption in the substrate is frequently used to limit the transmission range of the filter. Reflectance's at the filter interfaced need also to be considered. However, they can be reduced by antireflection coating, or by cementing several components together [19].

In general, a filter can consist of multilayer coatings deposited onto one or both side of a substrate. The overall transmittance Ttotal of a filter can be expressed in term of the internal or intrinsic transmittance (τ) of the substrate and transmittanceT1, T2 and internal reflectance's R1, R2 of each surface of the substrate.

The internal transmittance (τ) of the substrate is defined to be ratio of the intensity (T'') just before reaching the second interface to the intensity (T') just after entering the substrate.

$$\tau = \frac{T''}{T'} \qquad (2.10)$$

Providing that the incident light is not coherent, there will be no interference between the beams reflected from the two surfaces of the substrate, even when the surfaces are plane-parallel.

The summation of all the reflections' leads to the following expression for the overall spectral transmittance Ttotal of a filter [22].

$$T_{total} = \frac{T_1 T_2 \tau}{1 - R_1 R_2 \tau^2} \qquad (2.11)$$

The reflection coefficients of uncoated can be calculated providing that the complex refractive indices of the substrate and of the medium are known. If all the materials in the filter are non-absorbing, then

$$T_{total} = \frac{T_1 T_2}{1 - R_1 R_2} \qquad (2.12)$$

If R1 is small, an appropriate expression for Ttotal is

$$T_{total} \approx [1 - R_1(1 - R_2)]T_2 \qquad (2.13)$$

However, this last approximation is not valid in general; some infrared substrate materials have high reflection coefficients and such cases must be used

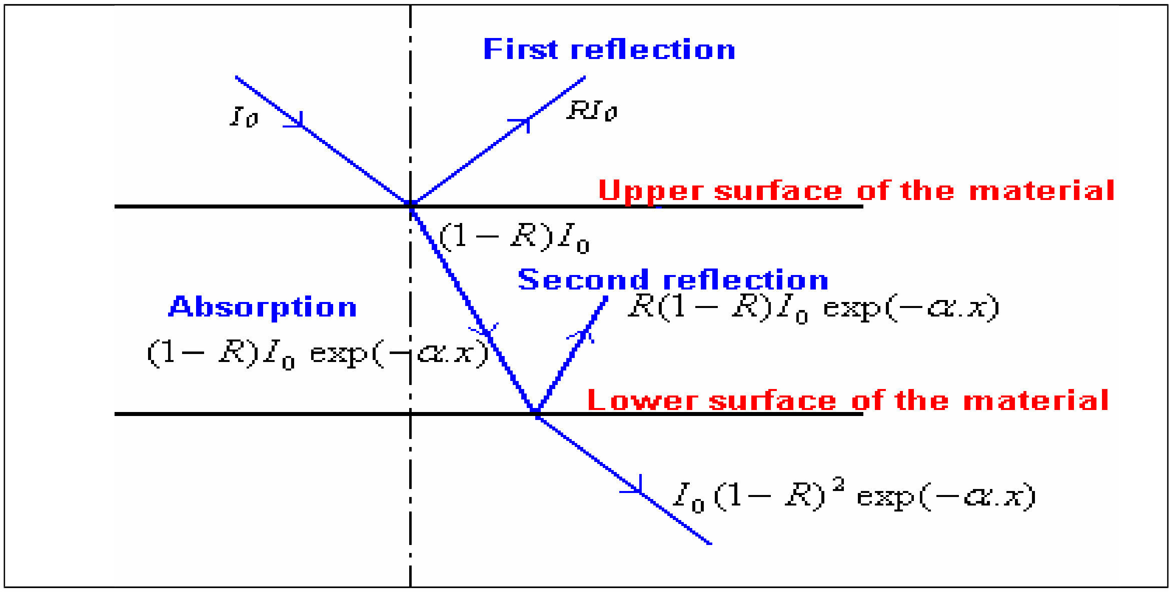

Figure 2.3 scheme of multilayer reflection [15].