CHAPTER ONE BASIC CONCEPTS

1-1 Introduction:

Virtually no modern optical system could operate without optical coating, much of any optical system consist of a series of coated and shaped surfaces. The shape determines the power of the surface but it's the coating that determines the specular properties, the amount of light transmitted or reflected, the phase change, the emittance, the color, the polarization, the retardation, including even the mechanical properties. Optical coating consist of assemblies of thin films of materials where interference properties combine with intrinsic properties of the materials to yield the desired optical performance. They act to reduce the reflectance losses of lenses; increase the reflectance of mirrors, reduce glare and electromagnetic emission from display systems, improve the thermal insulation of buildings, protect eyes from laser radiation, analyze gases, act as anti-counterfeiting devices on banknotes, multiplex or de-multiplex communication signals, separate or combine color channels in display projectors and these are just a few of their roles (Macleod, 2011).

Very thin layers of material that are deposited on the surface of another material (thin films) are extremely important to many technology-based industries. The deposition of thin films on a glass substrate can change physical properties of the specimen. One important factor that has a principal effect on the characteristic of a work piece is the thickness of the coated film. Film thickness has a direct effect on physical properties of the specimen such as optical transmission, reflection and electrical resistance. To study the optical properties of matter through spectroscopy, the electromagnetic radiation basic concepts, matter physical and chemical description are essential.

Spectroscopy is the study of the interaction between matter and electromagnetic radiation. Historically, spectroscopy originated through the study of visible light dispersed according to its wavelength, by a prism. Later, the concept was expanded greatly to comprise any

interaction with radiative energy as a function of its wavelength or frequency. Spectroscopic data is often represented by a spectrum, a plot of the response of interest as a function of wavelength or frequency (Self.gutenberg, 2015). Thus to deposit a thin films and to study its optical properties—requires reviewing matter and spectroscopy basic concepts. Among the variety of methods used for the growing of thin metallic films, high-vacuum thermal evaporation, has proved to be an efficient technique and widely used in both research and industry (Hernández et al., 1999). Optical techniques for film-thickness determinations are widely used because they are applicable to both opaque and transparent films and generally yield thickness values of high accuracy. In addition, measurements are rapidly performed, frequently nondestructive, and utilize relatively inexpensive equipment (Hernández et al., 1999)

The thickness of the film t can be calculated from the shift in interference fringes many papers exists in this topic, in this thesis a setup established in the work of Elhadi, S.E., (2007) will be used to determine the film thickness, and the transmission spectrum of the film will be obtained from measurement of the intensity of different laser systems that transmitted through the thin film, then optical constants such as refractive index will be calculated. Each technique has difference benefits and drawbacks. Normally, the selection is based on the type of the film, range, resolution and accuracy of the measurement (Hernández et al., 1999)

One of the most important optical constants of a material is its refractive index, which in general depends on the wavelength of the electromagnetic wave, through a relationship called dispersion. In materials, where an electromagnetic wave can lose its energy during its propagation, the refractive index becomes complex. The real part is usually the refractive index, n, and the imaginary part is called the extinction coefficient K (Jai Singh, 2006).

Optical properties of a material change or affect the characteristics of light passing through it by modifying its propagation vector or intensity. Two of the most important optical properties are the refractive index n and the extinction coefficient K, which are generically called optical constants (Jai Singh, 2006).

1-2 Study Objectives:

The objectives of this study are:

- Fabrication of single layer thin films of CuSO₄ on glass substrate by evacuation method.
- Determination of the thin films optical properties using transmission measurements.

1-3 Thesis structure:

This chapter presents the basic concepts related to thin film deposition, light nature, defined laser characteristics and optical characterization of thin films, a literature review was taken before starting this work, also this chapter reviews interference from thin film, define reflectivity of thin film on a substrate and discuss measurement techniques.

Chapter two cover the experimental part of this work, materials used and their specifications, a setup used to deposit the thin films.

Results and discussion are presented in chapter three, followed by conclusions and recommendations for future works.

1-4 Laser and its properties:

This section is not a review of the laser fundamentals, but only to mention that laser is a sort of light that exhibit certain characteristics.

The word laser is an acronym of the words: Light Amplification by Stimulated Emission of Radiation (Scitech.web.cern.ch, May 2015).

The three main components of any laser device are the active medium, the pumping source, and the optical resonator. The active medium consists of a collection of atoms, molecules, or ions (in solid, liquid, or gaseous form), which acts as an amplifier for light waves. For amplification, the medium has to be kept in a state of population inversion, i.e., in a state in which the number of atoms in the upper energy level is greater than the number of atoms in the lower energy level.

The pumping mechanism provides for obtaining such a state of population inversion between a pair of energy levels of the atomic system (K. Thyagarajan, Ajoy Ghatak, 2010). Laser light has four main characteristics that differentiate it from the light produced from, for example, an electrical light bulb:

• Coherent radiation comprises waves travelling with the same wavelength, amplitude and wavefront. It is a measure of the degree to which light waves are in phase in both time and space. Laser radiation has high coherence. Spatial coherence is a measure of the difference in the spatial position of waves. Coherent laser light is up to 100 000 times higher in intensity than incoherent light of equivalent power, since the divergence, or dispersion, of energy is very low as the beam propagates from the laser. Because light propagates with a fixed velocity, a temporal coherence can be defined, which is a measure of the difference in time between waves emitted from a single source that produce stationary interference patterns. Coherence is the basis of applications in measurement and holography (Ion, 2005).

- Laser light is highly monochromatic, that is, it has a very narrow spectral width. The spectral width is greater than zero, but typically it is much less than that of conventional light sources (Ready, 1997).
- The beam from the laser normally converges to a waist as it leaves the resonator, where its diameter is a minimum, after which it diverges along the beam path. The tendency for the beam diameter to expand away from the waist is a measure of the beam divergence. Low divergence is the property that enables a laser beam to retain high brightness over a long distance, and is the basis of alignment systems (Ion, 2005).
- The radiance of a light source is the power emitted per unit area per unit solid angle. The relevant solid angle is that defined by the cone into which the beam spreads. Lasers emit their light into very small solid angles, perhaps 10^{-6} steradians (sr) or less, whereas conventional light sources emit into a solid angle of 4π sr (Ready, 1997).

1-5Transparent and opaque materials:

A material that does not absorb significantly is said to be transparent (Tilley, 2011). Some matters allow most optical energy (all photons) to propagate through it and the matter in this case is called optically transparent. In contrast, some dense matters absorb light within the first few atomic layers and are called non-optically transparent or opaque matter (it scatters and / or absorbs the photons). Example: compare glass or water with a sheet of metal.

Some matters passes a portion of optical energy through it and absorbs part of it (typically ~ 50 %), and is called semitransparent matter. Such matter attenuates the optical power of light and may be used in optical devices known as optical attenuators. Example: most transparent matter, semitransparent mirrors.

Some matter allow selected frequencies to propagate through and is called an optical filter. Example: red, green, yellow, or blue glass (each allows a selected range of frequencies to be propagated through it).

Some matters in an ionized state absorb selected frequencies and pass all others. Example: the sun's ionized surface or the hot vapor of sulfur.

Some matters permit rays with certain polarization to propagate through and absorb or reflect the others; it is called a polarizing filter. Example: polarizing sunglasses.

Some matters emit photons when it is illuminated with light of another shorter wavelength. Example: most minerals under UV light; fluorescent substances, erbium, and so on (Palmer, 1995).

1-6 Homogeneity and heterogeneity:

Homogeneity and heterogeneity are concepts often used in the sciences and statistics relating to the uniformity in a substance or organism. A material or image that is homogeneous is uniform in composition or character (i.e. color, shape, size, weight, height, distribution, texture, language, income, temperature, radioactivity, architectural design, etc.); one that is heterogeneous is distinctly nonuniform in one of these qualities (Rennie &Richard,2003). Homogeneous medium is one in which n is everywhere the same. In an inhomogeneous or heterogeneous medium the index varies with position (Palmer, 1995).

1-6-1 Homogeneity:

It is the state of being homogeneous. Pertaining to the sciences, it is a substance where all the constituents are of the same nature; consisting of similar parts, or of elements of the like nature. For example, homogeneous particles, homogeneous elements, homogeneous principles, or homogeneous bodies; or (algebra) possessing the same number of factors of a given kind as with a homogeneous polynomial (Self.gutenberg, 2015).

1-6-2 Heterogeneity:

Is the state of being heterogeneous. It is the nature of opposition, or contrariety of qualities. It is diverse in kind or nature; composed of diverse parts, or resulting from

differing causes. In general, a heterogeneous entity is composed of dissimilar parts, hence the constituents are of a different kind that can be distinguished from one another. The parts (or constituents) are connected, and of a conglomerate mass, and viewed in respect to the parts of which it is made up.

Various disciplines understand heterogeneity, or being heterogeneous, in different ways. For example: **In physics**, it is understood as having more than one phase (solid, liquid, gas) present in a system or process. **In chemistry**, a heterogeneous material consists of either or both of **a**) multiple states of matter or **b**) hydrophilic and hydrophobic substances in one mixture; an example of the latter would be a mixture of water, octane, and silicone grease. Heterogeneous solids, liquids, and gases may be made homogeneous by melting, stirring, or by allowing time to pass for diffusion to distribute the molecules evenly. For example adding dye to water will create a heterogeneous solution at first, but will become homogeneous over time. Entropy allows for heterogeneous substances to become homogeneous over time (Self.gutenberg, 2015).

1-7 Isotropy and Anisotropy:

In an isotropic medium n is the same at each point for light traveling in all directions and with all polarizations, so the index is described by a scalar function of position. Isotropy is uniformity in all orientations; it is derived from the Greek isos (ἴσος, "equal") and tropos (τ ρόπος, "way") .Anisotropy (ænar sptrəpi) is the property of being directionally dependent, as opposed to isotropy, which implies identical properties in all directions. It can be defined as a difference, when measured along different axes, in a material's physical or mechanical properties (absorbance, refractive index, conductivity, tensile strength, etc.) An example of anisotropy is the light coming through a polarizer. Another is wood, which is easier to split along its grain than against it (Phys.org, 2015).

1-8 : Refractive index and extinction coefficient:

The refractive index of an optical or dielectric medium, n, is the ratio of the velocity of light c in vacuum to its velocity v in the medium; n = c/v. Using this and Maxwell's equations,

one obtains the well-known Maxwell's formula for the refractive index of a substance as $n = \sqrt{\varepsilon_r \mu_r}$, where ε_r is the static dielectric constant or relative permittivity and μ_r the relative permeability. As $\mu_r = 1$ for nonmagnetic substances, one gets, $n = \sqrt{\varepsilon_r}$, which is very useful in relating the dielectric properties to optical properties of materials at any particular frequency of interest. As ε_r depends on the wavelength of light, the refractive index depends on the wavelength of light, and this dependence is called dispersion. In addition to dispersion, an electromagnetic wave propagating through a lossy medium experiences attenuation, which means it loses its energy, due to various loss mechanisms such as the generation of phonons (lattice waves), photogeneration, free carrier absorption, scattering, etc. (Jai Singh, 2006).

In such materials, the refractive index becomes a complex function of the frequency of the light wave. The complex refractive index, denoted usually by n^* , with real part n, and imaginary part K, called the extinction coefficient, is related to the complex relative permittivity, $\varepsilon_r = \varepsilon_r' - j\varepsilon_r''$, by:

$$n^* = n - jK = \sqrt{\varepsilon_r' - j\varepsilon_r''}$$
 (1-1)

where ε_r' and ε_r'' are, respectively, the real and imaginary parts of ε_r , this equation gives:

$$n^2 - K^2 = \varepsilon_r'$$
, $2nK = \varepsilon_r''$ (1-2)

In explicit terms, n and K can be obtained as:

$$n = \frac{1}{\sqrt{2}} \left[\left(\varepsilon_r'^2 + \varepsilon_r''^2 \right) + \varepsilon_r' \right]^{\frac{1}{2}}$$
 (1-3)

$$K = \frac{1}{\sqrt{2}} \left[\left(\varepsilon_r'^2 + \varepsilon_r''^2 \right) - \varepsilon_r' \right]^{\frac{1}{2}} \tag{1-4}$$

The optical constants n and K can be determined by measuring the reflectance from the surface of a material as a function of polarization and the angle of incidence. For normal incidence, the reflection coefficient, r, is obtained as:

$$r = \frac{1 - n *}{1 + n *} = \frac{1 - n + jK}{1 + n - jK}$$
 (1-5)

The reflectance *R* is then defined by:

$$R = |r|^2 = \left| \frac{1 - n + jK}{1 + n - jK} \right|^2 = \frac{(1 - n)^2 + K^2}{(1 + n) + K^2}$$
 (1-6)

Notice that whenever K is large, for example over a range of wavelengths, the absorption is strong, and the reflectance is almost unity. The light is then reflected, and any light in the medium is highly attenuated (Jai Singh, 2006).

1-9 Interaction of light with matter:

The way that light interacts with a material can be described in terms of scattering or absorption. To a first approximation, scattering is well treated by assuming that the light behaves as an electromagnetic wave, while absorption is best treated in terms of photons. When light interact with matter the light can be reflected, absorbed or scattered. Some absorption centres are able to re-emit light as fluorescence or luminescence (Tilley, 2011). All of the processes are wavelength dependent and can lead to colour production, figure (1.1) shows schematically these processes. The different parts of the electromagnetic spectrum have very different effects upon interaction with matter. Starting with low frequency radio waves, the human body is quite transparent. As we move upward through microwaves and infrared to visible light, we absorb more and more strongly. In the lower ultraviolet range, all the UV from the sun is absorbed in a thin outer layer of your skin. As we move further up into the x-ray region of the spectrum, you become transparent again, because most of the mechanisms for absorption are gone. You then absorb only a small fraction of the radiation, but that absorption involves the more violent ionization events.

Each portion of the electromagnetic spectrum has quantum energies appropriate for the excitation of certain types of physical processes. The energy levels for all physical processes at the atomic and molecular levels are quantized, and if there are no available quantized energy levels with spacing's which match the quantum energy of the incident radiation, then the material will be transparent to that radiation, and it will pass through (R. Nave ,2015).

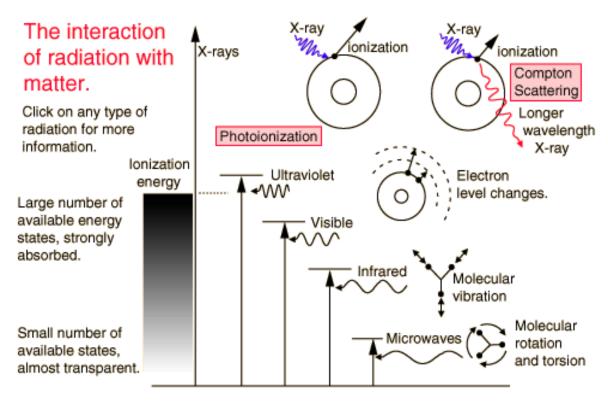


Fig.1.1: The interaction of radiation with matter

1-9-1 Absorption:

Absorption is the process by which incident radiant flux is converted to another form of energy, usually heat. Absorptance is the fraction of incident flux that is absorbed. The

absorptance α of an element is defined by $\alpha = \frac{\phi_a}{\phi_i}$. Similarly, the spectral absorptance $\alpha(\lambda)$ is the ratio of spectral power absorbed $\phi_{\lambda a}$ to the incident spectral power $\phi_{\lambda i}$,

$$\alpha = \frac{\int_{0}^{\infty} \alpha(\lambda)\phi_{\lambda i}d\lambda}{\int_{0}^{\infty} \phi_{\lambda i}d\lambda} \neq \int_{0}^{\infty} \alpha(\lambda)d\lambda$$
 (1-7)

An absorption coefficient α' (cm⁻¹ or m⁻¹) is often used in the expression $\tau_i = e^{-\alpha' t}$, where τ_i is internal transmittance and t is path length (cm or km) (Palmer, 1995).

1-9-1-1 Beer-Lambert Law:

As a beam of light passes through a material it gradually loses intensity, a process generally called attenuation (formerly extinction). Attenuation is due to the interaction of light with a material in two basic ways: scattering or absorption (Figure 1.2). When attenuation takes place in a homogeneous solid the amount of light transmitted by a semitransparent plate of thickness x is given by:

$$I_{x} = I_{0}e^{-\alpha_{e}x} \tag{1-8}$$

where I_x is the irradiance leaving the plate, I_o is the incident irradiance and α_e (m⁻¹) is the (Napierian) linear attenuation coefficient (formerly extinction coefficient). Equation (1.8) is known as Lambert's law or Beer's law, although it was first clearly set out by Bouguer and should, by rights, be called Bouguer's law (Tilley, 2011).

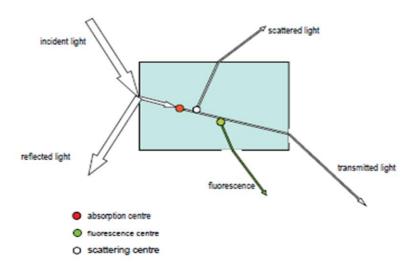


Fig.1. 2: The interaction of light with a transparent material. The light can be reflected, absorbed or scattered. Some absorption centres are able to re-emit light as fluorescence or luminescence. All of the processes labelled are wavelength dependent and can lead to colour production.

The fraction (in T units) of a collimated beam of light of wavelength (λ) transmitted through a material of index of refraction (n) and a thickness (t), (Justin Peatross & Michael Ware, 2011),

is given by:

$$I_{T} = \frac{I_{0}}{1 + \frac{4r^{2}}{(1 - r^{2})} \sin^{2}(\frac{2\pi nt}{\lambda})}$$
(1-9)

where $r^2 = R$ (the reflectance) given for normal incidence as:

$$R = \frac{(n-1)^2}{(n+1)^2} \tag{1-10}$$

1-9-2 Reflection:

Reflection is the process where a fraction of the radiant flux incident on a surface is returned into the same hemisphere whose base is the surface and which contains the incident radiation. The reflection can be specular (in the mirror direction), diffuse (scattered into the entire hemisphere), or a combination of both (Palmer, 1995). The most

general definition for reflectance ho is the ratio of the radiant flux reflected ϕ_r to the incident radiant flux ϕ_i , or

$$\rho = \frac{\phi_r}{\phi_i} \tag{1-11}$$

Spectral reflectance is similarly defined at a specified wavelength as:

$$\rho(\lambda) = \frac{\phi_r}{\phi_i} \tag{1-12}$$

1-9-3Emittance:

Emittance (ε) is the ratio of the radiance of an object or surface to the radiance of a blackbody (planckian radiator) at the same temperature. It is therefore dimensionless and can assume values between 0 and 1 for thermal radiators at equilibrium. Spectral emittance $\varepsilon(\lambda)$ is the emittance at a given wavelength. If a radiator is neutral with respect to wavelength, with a constant spectral emittance less than unity, it is called a graybody (Palmer, 1995).

$$\varepsilon = \frac{L}{L^{bb}} \quad \varepsilon(\lambda) = \frac{L_{\lambda}}{L^{bb}_{\lambda}} \tag{1-13}$$

where: L is the radiance of the object or surface, L^{bb} is the radiance of black body. Directional emittance $\varepsilon(\theta, \phi)$ was defined by:

$$\varepsilon(\theta, \phi) = \frac{L(\theta, \phi)}{L^{bb}} \tag{1-14}$$

Note that if the body is nongray, its emittance is dependent upon temperature inasmuch as the integral must be weighted by the source (Planck) function:

$$\varepsilon = \frac{\int_{0}^{\infty} \varepsilon(\lambda) L_{\lambda}^{bb} d\lambda}{\int_{0}^{\infty} L_{\lambda}^{bb} d\lambda} = \frac{1}{\pi} \int_{0}^{\infty} \varepsilon(\lambda) L_{\lambda}^{bb} d\lambda \tag{1-15}$$

1-9-4 Dispersion:

The variation of the refractive index of a transparent material with wavelength is known as dispersion (Figure 1.3). Dispersion can be formally defined as the slope of the refractive index n versus the wavelength λ curve, $\frac{dn}{d\lambda}$. In general, the index of refraction increases as the wavelength decreases, so that the refractive index of red light in a material is less than that of violet light. This situation is referred to as normal dispersion. Although the normal dispersion of many materials is rather small, it is important to include it when calculating the optical properties of lenses and similar high-quality optical components. Anomalous dispersion is found in the region of absorption bands in the material, when transparency is lost. These absorption bands are associated with transitions from one energy configuration (often the ground state) to higher energy levels (Tilley, 2011).

For many transparent materials a good representation of the variation of refractive index with wavelength in the visible region is given by Cauchy's equation:

$$n = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \tag{1-16}$$

where A, B and C are empirically determined parameters. For lens design Cauchy's equation is not sufficiently precise, and a more accurate formula, which gives the refractive index of glasses in the wavelength range 365- 2300 nm to high degree of fidelity, is the Sellmeier equation:

$$n = \left(1 + \frac{B_1 \lambda^2}{\lambda^2 - C_1} + \frac{B_2 \lambda^2}{\lambda^2 - C_2} + \frac{B_3 \lambda^2}{\lambda^2 - C_3}\right)^{\frac{1}{2}}$$
 (1-17)

where the wavelength λ is in micrometers and B_1 , B_2 and B_3 and C_1 , C_2 and C_3 are the Sellmeier constants appropriate to the glass. The Sellmeier equation can also be applied to transparent crystals (Tilley, 2011).

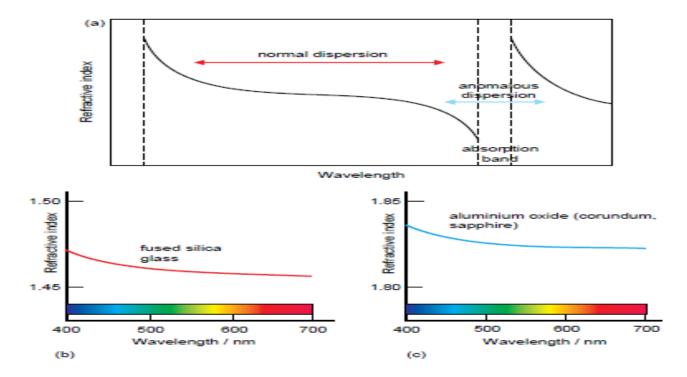


Fig.1.3: The variation of refractive index with wavelength. (a) Schematic dispersion curve for a transparent material. Anomalous dispersion occurs close to energy transitions from a lower to a higher energy level. (b) Dispersion curve for fused silica glass. (c) Dispersion curve for corundum, Al₂O₃. In the case of corundum the refractive index depends upon direction and average values are plotted.

1-9-5 Scattering:

Scattering is the interaction between radiation and matter which causes the photon to change direction. If the energy of the photon is the same before and after scattering, the process is called elastic or Rayleigh scattering (G. Gauglitz & T. Vo-Dinh, 2003). It was Lord Rayleigh in 1871 who showed that the intensity I_s of scattered light is related to λ by (Hollas, 2004):

$$I_s \propto \frac{1}{\lambda^4} \tag{1-18}$$

If the photon loses some of its energy, the process is called inelastic or Compton scattering (Dale et al., 2012). Compton scattering, or shift, is given by:

$$\Delta \lambda = (\lambda' - \lambda) = \frac{h}{m_0 c} (1 - \cos \theta) \tag{1-19}$$

where θ is the angle of scattering, h is Planck's constant, c is speed of light in vacuum and m_0 is the rest mass. More important scattering phenomenon is Raman Scattering. Raman spectroscopy is based on the Raman scattering phenomenon of electromagnetic radiation by molecules (Yang Leng, 2008). When irradiating materials with electromagnetic radiation of single frequency, the light will be scattered by molecules both elastically and inelastically.

1-9-6 Kirchhoff's Law:

In a closed system at thermal equilibrium, conservation of energy necessitates that emitted and absorbed fluxes are equal. Since the radiation field in such a system is isotropic (the same in all directions), the directional spectral emittance and the directional spectral absorptance must be equal, i. e.,

$$\varepsilon(\lambda; \theta, \phi) = \alpha(\lambda; \theta, \phi) \tag{1-20}$$

This statement was first made by Kirchhoff (1860). Strictly, this equation holds for each orthogonal polarization component, and for it to be valid as written, the total radiation must have equal orthogonal polarization components. Kirchhoff's law is often simplified to the declaration $\varepsilon = \alpha$; however, this is not a universal truth; it may only be applied under a limited set of conditions (Palmer, 1995).

1-10 Relationship between Transmittance, Reflectance, and Absorptance:

Radiant flux incident upon a surface or medium undergoes transmission, reflection, and absorption (Palmer, 1995). Application of conservation of energy leads to the statement that the sum of the transmission, reflection, and absorption of the incident flux is equal to unity, or

$$\alpha + \tau + \rho = 1 \tag{1-21}$$

In the absence of nonlinear effects (i.e., Raman Effect, etc.),

$$\alpha(\lambda) + \tau(\lambda) + \rho(\lambda) = 1 \tag{1-22}$$

If the situation is such that one of the above Kirchhoff-type relations is applicable, then emittance ε may be substituted for absorptance α in the previous equations, or

$$\varepsilon = 1 - \tau - \rho$$
, $\varepsilon(\lambda) = 1 - \tau(\lambda) - \rho(\lambda)$ (1-23)

1-11 Intensity Measurement:

An intensity measurement is obtained by converting the intensity into voltage through a shunt resistance. The voltmeters then measures the voltage to the resistance limits. The important parameter to consider in estimating the quality of the measurement is the voltage drops to the limits of the shunt resistance (Dominique Placko, 2007).

Upon interacting with a sample, incident light of intensity I_0 may be partly reflected at optical interfaces (I_R), it may be scattered (I_S) and absorbed in the sample (I_A), the remaining part will be transmitted (I_T), this is shown in Fig. (1.4) (Palmer, 1995):

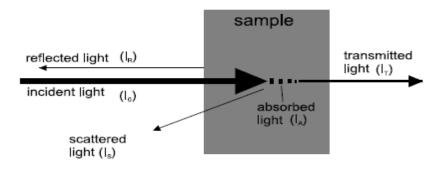


Fig.1.4: Energy balance of incident light upon interaction with a sample.

According to the law of conservation of energy, the energy balance for the incident light may be written as:

$$I_0 = I_A + I_S + I_R + I_T ag{1-24}$$

The light intensities I_0 , I_T , I_R and I_s can easily be measured by placing a detector at the corresponding position. All the information about the sample goes into I_A , but this value cannot be measured directly. I_A can only be accessed by evaluating Eq. (1.24),

(Palmer, 1995). Table 1.1 lists the measurement techniques and the evaluation for transmission, reflection and diffuse reflection measurement.

Table 1.1: Measured and illicit contributions of light.

Measured	Aim of Sample Preparation	Evaluation	Exp. Technique
I_0 , I_{T}	$I_{R} = I_{S} = 0$ $I_{R} = I_{R} = 0$	$I_{A} = I_{0} - I_{T}$	Transmission measurements Reflection measurements
I_0 , I_R I_0 , I_S	$I_{\rm T} = I_{\rm S} = 0$ $I_{\rm T} = I_{\rm R} = 0$	$I_{A} = I_{0} - I_{R}$ $I_{A} = I_{0} - I_{S}$	Diffuse reflection measurements

1-11-1 Transmission measurement:

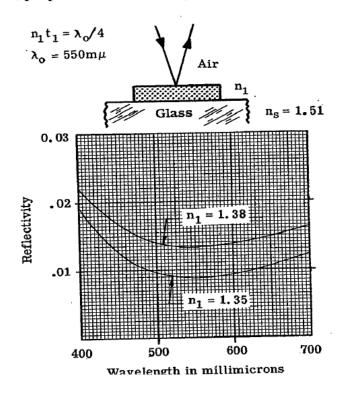
Transmission spectroscopy is the most widely used measurement technique. It is simple and can be applied to characterize gases, liquids and solids. Quantitative evaluations are based on the Beer Lambert law as described above. Polished windows must not be touched or even scratched. Fingerprints in the light path cause light scattering, hence reducing the accuracy of the measurement. Normal incidence of the incoming light is required in order to minimize reflection (Palmer, 1995).

1-12 Single and Multi-Layer Thin films:

A thin film is a layer of material with thickness in the sub-nanometer to micron range (Gmb,2015). As light strikes the surface of a film it is either transmitted or reflected at the upper surface. Light that is transmitted reaches the bottom surface and may once again be transmitted or reflected. The Fresnel equations provide a quantitative description of how much of the light will be transmitted or reflected at an interface. The light reflected from the upper and lower surfaces will interfere. The degree of constructive or destructive interference between the two light waves depends on the difference in their phase. This difference in turn depends on the thickness of the film layer, the refractive index of the film, and the angle of incidence of the original wave on the film. Additionally, a phase

shift of 180° or π radians may be introduced upon reflection at a boundary depending on the refractive indices of the materials on either side of the boundary (Boundless, 2015). This phase shift occurs if the refractive index of the medium the light is travelling through is less than the refractive of the material it is striking. In other words, if the light is travelling from material 1 to material 2, then a phase shift occurs upon reflection. The pattern of light that results from this interference can appear either as light and dark bands or as colorful bands depending upon the source of the incident light (Tilley, 2011).

Quite frequently optical components are coated with thin layers of various solid materials for the purpose of altering either their physical or optical properties. As an example of the former purpose, aluminum mirrors are often coated with a thin layer of silicon monoxide in order to increase their resistance to abrasion and chemical attack. The addition of this layer alters the spectral reflectivity of the mirrors, although this is not the primary purpose of such a coating, figure (1.5 (a), (b) and (c)) shows a light of a given wavelength fall on a single layer thin film that are deposited on glass substrate of different refractive indices and the computed spectral reflectivity in each case (fp.optics.arizona,2015).



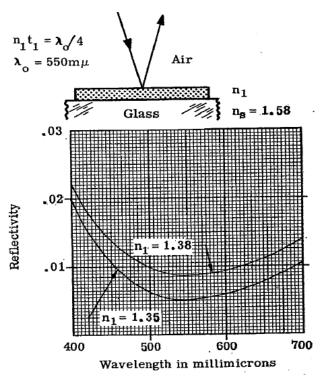


Fig.1.5: (a) the spectral reflectivity of single layer at normal incident $n_s = 1.51$, (b) the spectral reflectivity of single layer at normal incident $n_s = 1.58$, the film material is MgF whose index of refraction is 1.38.

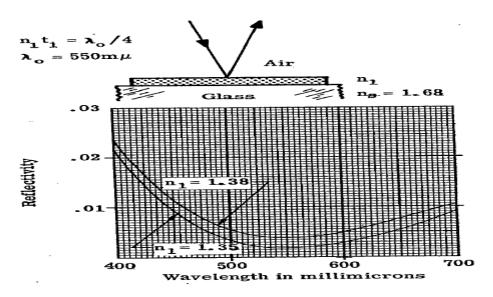


Fig.1.5: (c) the spectral reflectivity of single layer at normal incident $n_s = 1.68$.

More frequently, however, thin film coatings are used for the primary purpose of altering the spectral reflection and transmission of optical components. Sometimes a thin film coating consist of only one layer deposited upon a suitable substrate. In other cases, many layers, often as many as forty or fifty, are used to produce a given optical filter. Hence this type of filter is called a multilayer filter, or simply a multilayer (fp.optics.arizona,2015).

Traditionally, mirrors have been made from metals. The best metallic mirrors are made of a thick layer of silver, which has a reflectivity of about 0.96 in the visible. Surprisingly, multiple thin films of transparent materials can be laid down one on top of the other in such a way as to form perfect mirrors. These are often called dielectric mirrors. The fabrication of such devices forms part of the subject area known as photonic or thin-film engineering. A wide variety of multilayer mirrors are now manufactured, mainly from oxides and fluorides. These are all stable in air and have the additional advantage over metallic mirrors of not degrading in normal use.

The simplest formula for the reflectance of such a mirror refers to the specific case in which all layers are $\lambda/4$ thick and of alternating high (H) and low (L) refractive indices, n_H and n_L , illuminated by light falling perpendicular to the surface. The arrangement (Figure 1.6) is called a quarter-wave stack (Tilley, 2011). The maximum reflectance of a quarter-wave stack deposited on a substrate in the sequence:

substrate; L; H; L; H; L; H; . . . L; H; air

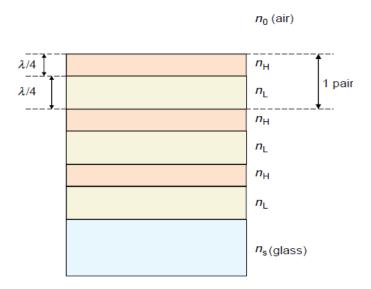


Fig.1.6: A stack of thin films, each of optical thickness $\lambda/4$, called a quarter-wave stack, can act as an effective dielectric mirror. The reflectivity increases with the number of pairs of layers and rapidly approaches 1.0.

1-13 Production methods of thin-films:

Manufacturers seeking to apply thin films have a host of deposition methods available to them, but the ideal method for a given application depends on the purpose of the deposition, the surface makeup of the substrate, and the thickness desired. There are basically two methods of deposition: chemical or physical (thomasnet.com, 2013).

1-13-1Chemical Deposition:

Chemical deposition is a process by which a substrate is fully submerged in a chemical fluid and then the material is deposited on the surface is a conformal pattern. This means every surface of the substrate is equally coated. The most common types of chemical deposition are :

1-13-1-1Plating:

In the plating process, a substrate is submerged in a chemical bath, often composed of water mixed with metal salts destined for deposition. The metal salts adhere to the substrate in a uniform pattern, building up a thicker film the longer the substrate is submerged. A more specialized form of plating, known as electroplating, requires the use of electricity. The substrate is connected to an anode powered by an external battery or rectifier. When the electricity is turned on, the metal particles in the liquid begin adhering to the substrate surface through oxidation. Although different metals adhere at varying speeds and thicknesses, the general rule for electroplating is the higher the charge and the longer the current is connected, the thicker the deposition coating (thomasnet.com, 2013).

1-13-1-2 Chemical Solution Deposition (CSD):

CSD is a process very similar to plating, except that instead of metal salts in a water bath, organometallic powders in an organic solvent carry out the deposition procedure. CSD is cheaper and simpler than plating techniques, although its results are comparable (thomasnet.com, 2013).

1-13-1-3 Chemical Vapor Deposition (CVD):

CVD does not use a liquid bath, but rather involves a substrate placed in a pressurized chamber full of organometallic gas. Typical organometallic gasses include polysilicon, silicon dioxide and silicon nitride. The gas either reacts with the substrate surface or slowly dissolves over it, depositing the thin film evenly. A more specialized variant of CVD is plasma enhanced CVD. Plasma is an ionized vapor, and is attracted to the surface of a substrate when excited by electric currents or microwave (thomasnet.com, 2013).

1-13-2 Physical Deposition:

Physical deposition techniques do not include chemical reactions. They rely on mechanical or thermodynamic methods to produce thin films instead. Generally, they require low-pressure environments for accurate and functional results (thomasnet.com, 2013).

1-13-2-1Thermal evaporation

In a high vacuum, the deposition material is melted by an electric resistance heater until it covers the surface of the substrate. The vacuum is required to make sure there is not an unwanted reaction between the film material atoms and gas atoms. A variant of thermal evaporation uses an electron beam evaporator to melt materials on a substrate. Because of the added precision, materials of lower vapor pressure can be melted than in standard thermal evaporation (thomasnet.com, 2013).

1-13-2-2 Sputtering

Sputtering occurs when a noble gas plasma is shot at a substrate in atom-sized particles. The impact of the particles triggers a collision cascade, which results in many of the particles passing through the substrate and adhering to the opposite side. In this manner, the entire surface of a substrate is coated (thomasnet.com, 2013).

1-13-2-3 Pulsed Laser Deposition:

Pulsed laser deposition involves a substrate and a block of film material in an ultra-high vacuum chamber. A laser fires pulsed bursts of light at the block of material, which vaporizes and transfers to the substrate facing it. Sometimes the pulsed laser deposition takes place in an oxidated chamber so that oxygen can aid in oxide deposition (thomasnet.com, 2013).

1-13-2-4 Cathodic Arc Deposition (Arc-PV):

Arc-PVD is very similar to pulsed laser deposition, except an electric arc is used instead of a pulsed laser. An electric arc is an electrical charge of a gas between an anode and a cathode, with the substance material serving as the cathode in Arc-PVD. As the

substance material vaporizes, it condenses on the substrate and forms a thin film (thomasnet.com, 2013).

1-13-3 Deposition from Liquid:

Liquid phase deposition (LPD) method is a useful method to create thin oxide films from aqueous solutions under ambient conditions (Valiulis A.V. and Silickas P., 2007). In this procedure the substrate is either dipped in an organo-metallic solution and withdrawn at a very steady rate from it, or the solution is applied from a pipette onto a spinning substrate. The substrate is then placed in an oven to drive off the solvent. The thickness of the film depends on the concentration of the solvent and on the rate of withdrawal or spinning. Other factors which influence the process are temperature and humidity, as well as the freshness of the solution. Although it yields quite porous films, this method is of interest because many of the layers produced in this way have a high laser damage threshold. The process has also been adapted for the coating of quite large area substrates with multilayer antireflection coatings for picture frame glass and for display windows (Farrow., 2009).

1-14 Interference by thin films:

When light waves from two coherent sources mix up and cross each other's path then a modification of intensity of light will occur in the region of crossing. This modification in the distribution of light energy obtained by the superposition of two or more waves is called interference (Uma Mukherji, 2007).

Generally in terms of path difference the condition for constructive interference is:

Path difference =
$$\Delta = (x_2 - x_1) = n\lambda$$
 (1-25)

And for destructive interference is:

Path difference =
$$\Delta = (x_2 - x_1) = (2n \pm 1)\frac{\lambda}{2}$$
 (1-26)

Newton and Hooke observed and developed an interference phenomenon due to multiple reflections from the surface of thin transparent materials. In daily life, we are familiar with the colours produced by the thin film of oil on the surface of water, by a thin film of a soap bubble and also in thin films of mica. Young was able to explain this phenomenon on the basis of interference between light reflected from the top and the bottom surface of a thin film. It has been observed that the interference in the case of thin film takes place due to: (1) reflected lights and (2) transmitted light from the top and bottom surface of the thin film (Uma Mukherji, 2007).

1-14-1 Thin film interference due to reflected light (Parallel Thin Film):

Consider a transparent parallel film (Fig.1.7) of the thickness t and refractive index μ . A ray SA incident on the upper surface of the film is partly reflected along AR₁ and partly refracted along AB, At B, part of its intensity reflected along BC and finally emerges out along CR₂ parallel to AR₁. This will continue further in the same way.

Thus for a single incident ray a number of parallel reflected rays like AR₁, CR₂ from the front surface and back surface of the film can be obtained. Similarly a number of parallel rays can be obtained from the transmitted portion of the incident rays like BT₁, DT₂. These parallel reflected rays having effective path difference in between themselves which cause interference, because they are all coherent (Uma Mukherji, 2007).

To determine the optical path difference: Draw CN normal to AR₁ and AM normal to BC, as shown in Fig. (1.6) the angle of incidence is i and the angle of refraction is r. Produce CB backward to meet AE at P. Hence $\angle APC = r$. So from $\triangle ABP$, AB=BP and AE=EP=t.

The optical path difference between AR₁ and CR₂ is:

$$\Delta = \mu[(AB + BC)] - AN$$

$$\mu = \frac{\sin i}{\sin r} = \frac{AN / AC}{CM / AC} \qquad \text{(from } \Delta ACN \text{ and } \Delta CAM \text{)}$$

Hence

$$\mu = \frac{AN}{CM} \qquad (:: AN = \mu CM)$$

$$\Delta = \mu(AB + BC) - \mu CM = \mu(AB + BC - CM)$$

$$= \mu(PB + BC) - \mu CM = \mu(PC - CM) \qquad (:: AB = BP)$$

$$:: \Delta = \mu PM$$

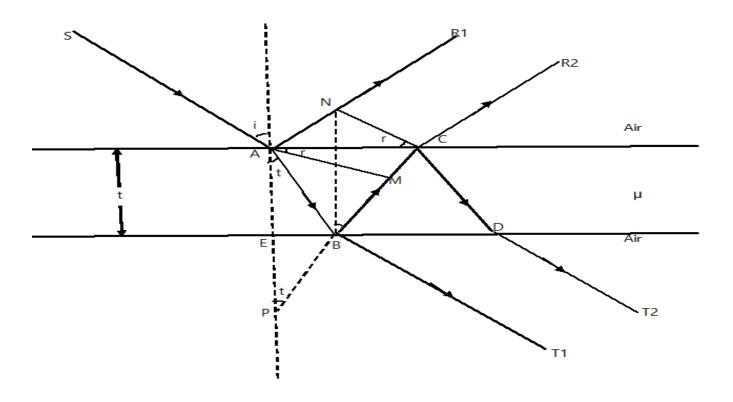


Fig.1.7: Optical path difference in parallel thin films for reflected beams.

In $\triangle APM$, $\cos r = PM/AP$, $PM = AP \cos r = (AE + EP) \cos r$

PM=2t cos r (:: AE = EP= t)
So
$$\Delta = \mu PM = 2 \mu t \cos r$$
 (1-27)

Above equation in the case of reflected light does not represent the correct path difference between two reflected rays AR_1 and CR_2 but only the apparent. It has been established on the basis of electromagnetic theory that, when light is reflected at point A, from the surface of an optically denser medium (Air medium interface) a phase change π , equivalent to path difference $\lambda/2$, occurs.

Therefore, the correct path difference in this case will be:

$$\Delta = 2\,\mu \quad t\cos r \pm \frac{\lambda}{2} \tag{1-28}$$

Condition for bright band in thin film for reflected light:

If the path difference, from the last equation (eq. 1-25) be $\Delta = n\lambda$, where n=0, 1, 2,... etc.

Then constructive interference takes place in case of thin film appears bright when:

$$2\mu \quad t\cos r \pm \frac{\lambda}{2} = n\lambda$$

Therefore

$$2\mu t \cos r = (2n \pm 1)\frac{\lambda}{2}$$
 (1-29)

Condition for dark band in thin film for reflected light:

If the path difference, from eqn.(1-26) be $\Delta = (2n \pm 1)\frac{\lambda}{2}$, where n=0, 1, 2,...etc. Then the destructive interference takes place and film appears dark when:

$$2\mu \quad t\cos r \pm \frac{\lambda}{2} = (2n \pm 1)\frac{\lambda}{2}$$

$$2\mu t \cos r = n\lambda or (n+1)\lambda$$

Hence n is an integer only. So (n+1) can also be taken as n:

$$2\mu \quad t\cos r = n\lambda \tag{1-30}$$

The condition for bright and dark band in thin film interference (eqns. 1-29 and 1-30) are just opposite to the general conditions (eqns. 1-25 and 1-26) for interference. That is, due to the extra phase difference of π occurs at reflection at A (Uma Mukherji, 2007).

1-14-2 Thin film interference due to transmitted light:

Figure 1.8 shows the geometry of the transmitted light due simultaneous reflection and refraction we obtain here two transmitted rays BR and DQ. These rays have originated from the same point source S hence they have a constant phase difference and are in a position to produce sustained interference when combined (Uma Mukherji, 2007).

The effective path difference between the rays BR and DQ is the path difference:

$$\Delta = \mu(BC + CD) - BN$$

But
$$\mu = \frac{\sin i}{\sin r}$$

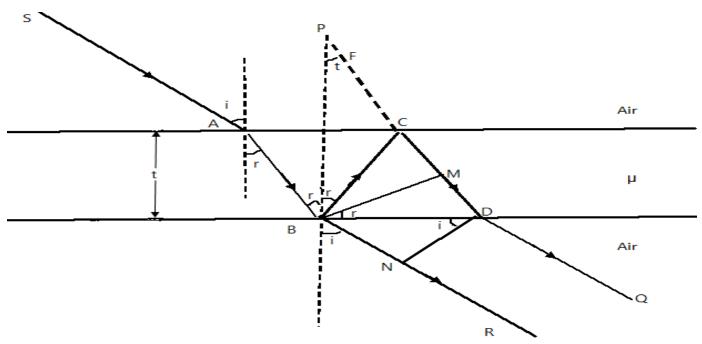


Fig.1.8: Optical path difference in parallel thin films for transmitted beams From Δ BMD and Δ BDN (where BM and DN are perpendicular on CD and BR, respectively, we get):

$$\mu = \frac{(BN/BD)}{(MD/BD)} = \frac{BN}{MD.BN} = \mu MD$$

Thus
$$\Delta = \mu(BC + CD - MD) = \mu(CP + CD - MD)$$
 (: $BC = CP$)

$$\Delta = \mu(PM)$$

But from \triangle BPM:

$$\cos r = \frac{PM}{PB.PM} = PB \cos r$$

i.e.,
$$PM = 2 t \cos r$$
 (:: $PB = 2t$)

So, path difference between BR and CQ is:

$$\Delta = \mu P M = 2\mu t \quad \cos \quad r \tag{1}$$

31)

Here it should be mentioned that inside the films, reflection at different points (say at B and C), takes from the surface of the rarer medium (air), thus no extra phase change π takes place in this case :

So condition for bright band in transmitted light is:

$$2\mu t \quad \cos \quad r = n\lambda \tag{1-32}$$

Condition for dark band in transmitted light is:

$$2\mu t \quad \cos \quad r = (2n \pm 1)\frac{\lambda}{2} \tag{1-33}$$

1-15 Reflectivity of a Single Thin Film on a Substrate:

The reflectivity of a single thin film deposited on a substrate, like that of a single thin film in air, depends upon the polarisation of the light, the film thickness and direction of the incident radiation (Tilley,2005) . In the case of monochromatic illumination perpendicular to a homogeneous nonabsorbing thin film:

$$R = \frac{2r_1^2 + 2r_1r_2\cos^2\delta + r_2^2}{1 + 2r_1r_2\cos^2\delta + r_1^2r_2^2}$$
(1-34)

where

$$r_1 = \frac{n_0 - n_f}{n_0 + n_f}$$

$$r_2 = \frac{n_f - n_s}{n_s + n_f}$$

 n_0 is the refractive index of the surrounding medium, n_f is the refractive index of the film and n_s is the refractive index of the substrate (Tilley, 2011). The expression for is δ :

$$\delta = \frac{2\pi[d]}{\lambda} = \frac{2\pi n_f d}{\lambda} \tag{1-35}$$

where [d] is the optical thickness of the film and d is the physical thickness of the film. For values of [d] given by, $\lambda/2$, λ , $3\lambda/2$ etc., the equation reduces to:

$$R = \frac{(n_0 - n_s)^2}{(n_0 + n_s)^2} \tag{1-36}$$

This is identical to the equation for an uncoated surface. Thus, a layer of optical thickness $\lambda/2$ etc. can be considered to be optically absent and the surface has normal uncoated reflectivity. This is an intriguing and a $\lambda/2$ layer of a hard transparent material the surface will be protected without any effect on optical properties (Tilley, 2005).

For values of [d] given by useful result. It means that if a delicate surface is coated with a $\lambda/4$, $3\lambda/4$, etc. the reflectivity is given by:

$$R = \frac{(n_f^2 - n_0 n_s)^2}{(n_f^2 + n_0 n_s)^2}$$
 (1-37)

and the reflectance will be either a maximum or a minimum. This will depend upon whether the film has a higher refractive index than the substrate or a lower refractive index than the substrate. When the refractive index of the film is between that of the surrounding medium and the substrate ($n_0 < n_f < n_s$), the reflectivity will be a minimum. When the film has a higher refractive index than both the substrate and the surrounding medium ($n_0 < n_f > n_s$), the reflectivity will be a maximum.

As with a thin film in air, the value of the reflectivity will cycle with film thickness between a lower value at [d] equal to 0, $\lambda/2$, λ , etc. to a maximum for values of [d] equal to $\lambda/4$, $3\lambda/4$ and so on. Because the refractive indices are a function of wavelength, the reflectivity will also vary across the spectrum (Tilley, 2011).

The absorption coefficients can be neglected in the case of thin films due to its short dimensions. Thus equation (1.22) can be written as $\tau(\lambda) + \rho(\lambda) = 1$, simply,

$$T + R = 1 \tag{1-38}$$

1-16 Typical Applications of thin Films:

Below are typical applications of thin films:

1-16-1 Antireflection coatings:

Whenever light traverses between two media of different refractive index, such as an air-glass interface of a lens, some of the light is reflected. Often the spacing of optical elements is such that these reflections are manifested in the image plane as "flare images". Before the advent of antireflection coatings, many otherwise acceptable lens configurations were rejected because they produced these flare images. The coating of optical surfaces with antirelection coatings has practically eliminated this problem. It is important that antireflection coatings be applied to infrared optical components, such as lenses or domes, which contain germanium, silicon, or other materials with a high refractive index. The loss of light at uncoated surfaces would be prohibitive otherwise (Cvilaseroptic, 2015).

1-16-2 Achromatic beam splitters:

Many optical devices, such as interferometers, range finders, optical gun sights, utilize beam splitters which divide a light and divert it into two directions. Thin metal films have been used as beam splitters for many years, but they are inefficient because the metal absorbs part of the light. More recently, multilayer beam splitters have been developed which are much more efficient, because they contain nonabsorbing materials. Less than one percent of the light is absorbed in a typical multilayer beam splitters; the remaining 99% of the light is either reflected or transmitted (fp.optics.arizona,2015).

1-16-3 Color filters and band-pass filters:

Multilayer filters are used to transmit (or "pass") a broad band of wavelengths in one spectral region, but attenuate in other regions. For example, a multilayer filter is available which transmits more than 90% in the blue but has a transmission of less than 0.5% in the green and red. This multilayer filter is superior to the conventional glass or dye-gelatin absorption filters, which has a much lower in the blue. Similar types of band-pass filters have been developed for the ultraviolet and infrared spectral regions. The spectral

transmission of some typical multilayer filters is shown in Figures (1.9 - 1.11) (fp.optics.arizona,2015); (Tilley, 2005).

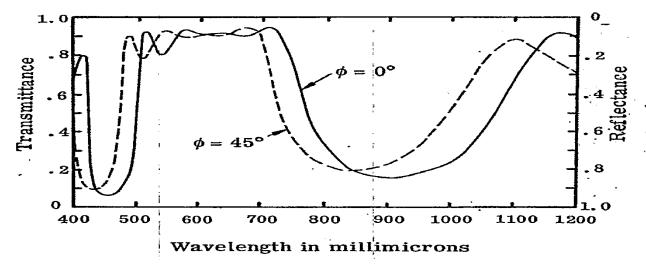


Fig.1.9: Measured spectral transmittance multilayer which reflects the blue and near infrared

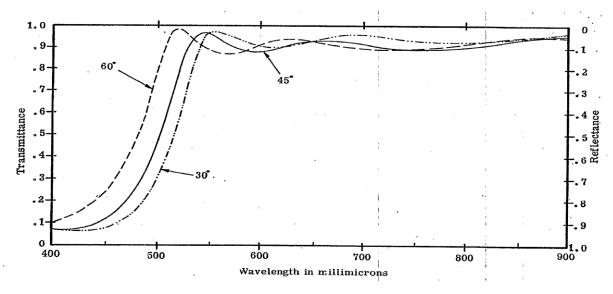


Fig.1.10: Measured spectral transmittance at various φ of a color selective beam splitter.

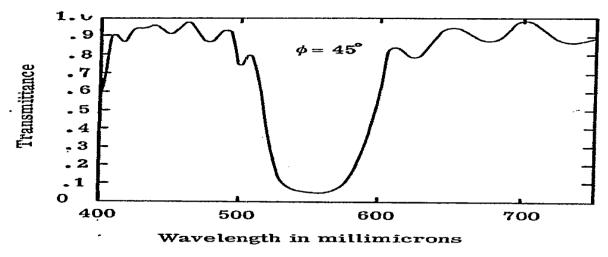


Fig.1.11: Measured spectral transmittance at ϕ =45° of a color selective beam splitter which reflects the green

1-16-4 Color-selective beam splitter:

Figure 1.12 shows a multilayer which is used as a color-selective beam splitter. In this example, the beam splitter transmits light, but reflects the green and red. Such beam splitters are useful as color separation devices in color photography and color television. This type of beam splitter is often called a dichroic mirror.

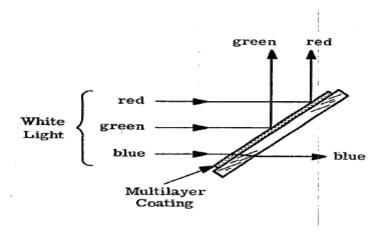


Fig.1.12: A color selective beam splitter which reflects the red and green, but transmits the blue.

1-16-5 Narrow pass-band (interference) filters:

Multilayer filters are used to transmit a narrow band of wavelengths, these narrowband filters are called interference filters, although in a technical sense all multilayer filters are interference filters, because they depend on the interference of light reflected from the various films. One type of interference filters which is manufactured commercially in large quantities has a pass band which is from ten to twenty millimicrons wide in the visible spectral region.

Custom- made filters have been produced which have a pass band as narrow as 0.1mµ. A filter of this type has been used to isolate one of the D lines at 589.0 mµ from its neighbor at 589.6 mµ. Such filters have many potential uses in the field of spectrochemical analysis.

1-16-6 Semi-transparent mirrors:

Multilayer mirrors have been produced which not only have a high reflectivity, but also transmit almost all of the light which is not reflected with a small absorption loss. A typical multilayer mirror might reflect 95% of the incident light and transmit 4.5%, the remaining 0.5% being absorbed or scattered. These multilayer mirrors have a much lower (absorption) loss than the conventional semi-transparent films of silver or aluminum and are useful for coating the plates of Fabry-Perot interferometer or the ends of the optical Laser. The spectral reflectivity of semi-transparent metal mirror is usually quite "flat", whereas the reflectivity of a typical multilayer mirror changes quite rapidly with wavelength (fp.optics.arizona,2015); (Tilley, 2005).

1-16-7 Heat control filters:

One type of a multilayer mirror, called a cold mirror, is used to reflect the visible light and transmit the infrared. Another type of heat control filter is the cover glass which is placed over solar cells which are used to power a space vehicle. These cover glasses are designed to reflect the radiant energy at wavelengths longer than 1.2 μ . The radiant energy from the sun in the wavelength from 1.2 μ to 2.5 μ does not generate power, but only increases the temperature of the solar cell, thereby decreasing its efficiency (Comaroptics,2013)

1-16-8 High reflectivity mirrors:

By overcoating aluminum and other metals with dielectric films, it is possible to obtain reflectivity as high as 99.5% (fp.optics.arizona,2015).

1-16-9 Polarizers:

Multilayers can be used to produce linear polarized light. They are particularly useful in the infrared, where conventional polarizers which utilizes birefringence cannot be used because most optical materials are optically isotropic.

1-16-10 Reflection filters:

A multilayer has been developed which has a high reflectivity in certain spectral regions, but absorbs strongly in the other regions. Such a mirror has been used to absorb the visible light and reflect the infrared (fp.optics.arizona,2015).

1-17 Literature Review:

Elhadi, S. E. in 2007 deposited a single layer thin film of a Chloroform and Rhodamine 6G on glass substrate at different temperatures and studied their optical properties. Thin films thicknesses in this work was determined from the interference fringes, monitored by C.R.O. The optical properties for these thin films were determined making use of their thicknesses.

Hernández M., in 1999, built a high-vacuum thermal evaporation system that allows growing up thin films for a variety of applications. For example metallic films grown up have been used as telescope mirror layers and for semi-mirrors as UV radiation filters. However, it was necessary to develop an alternative method which allows knowing the thickness of the film that has been grown up.

In their work, they report the results of measurements of thin films thickness, grown up on glass substrates by using an optical arrangement which uses an interferometer and a laser as a source of radiation. Comparison between two patterns of interference was taken into a count for the measurement of film thickness. These patterns were generated by

substrate without and with film. A Helium-Neon laser with a wavelength of 632.8 nanometers was applied as a source of radiation. The optical system applied to measure the thickness of the films uses a Michelson interferometer with even arms.

Valiulis A.V. and Silickas P. in 2007, tried to elucidate the role of the substrate during LPD (Liquid phase deposition) of TiO2 films by using Kapton with different types of surface treatments, SEM analysis showed that the deposited, LPD was used for Titania Deposition and Characterization, Given their relatively low acidity and low temperature, LPD methods are ideally suited to polymer substrates. The thickness of the Titania coating was determined by cross-sectional SEM. SEM images shows that samples ranging in thicknesses from 200–500 nm. EDAX (EDAX, is an instrumentation company providing Energy-Dispersive X-ray spectroscopy microanalysis, electron backscatter diffraction and micro- x-ray fluorescence systems) verified the identity of the Titania layer and its thicknesses could be directly determined from the SEM images. They conclude that the low-cost and convenience of LPD coatings and their lack of line-of-site limitations strongly recommend their being considered as a general strategy. Moreover, the relatively mild conditions for ceramic film formation using LPD methodology makes them prime candidates for application on polymer substrates.

Sangamesha M.A. et al. in 2013 were deposited thin films of Copper sulphide on glass substrates using chemical bath deposition technique at room temperature from the aqueous solution containing different concentration of copper sulphate between 0.05M and 0.15M. The effects of the copper concentration of the chemical bath on structural and optical properties of the amorphous thin film were investigated and discussed. The optical absorption and transmission of the thin films were observed between of 330-1100nm taken at room temperature. The optical band gaps of the as-synthesized copper sulphide thin film for various concentrations were measured. The surface morphology has been observed using scanning electron microscopy (SEM) and atomic force microscopy

(AFM). The results obtained from AFM demonstrated that the reflectivity was closely related to the surface roughness of the film. High surface roughness has a strong scattering effect on light and lowers the reflectivity. X-ray diffraction (XRD) patterns show that crystallinities of the films are dependent on the copper concentration in the solution.

Simion Jitian in 2011, worked on amorphous lead selenide film and it was obtained by chemical deposition on glass substrate from a solution of selenium sulfate and lead acetate, in his work he was measured the transmittance values in IR reflection-absorption (RA) spectra that were recorded using the specular reflection device of the spectrograph UR-20 Carl Zeiss Jena. A non-polarized infrared radiation was used and the obtained values were used to determine the optical constants of dielectric films laid on solid substrates. When the recorded spectra show interference fringes, the reflection-absorption spectra of PbSe recorded at 20 degrees and 55 degrees incidence angles. These spectra present interference fringes and were used to determine the thickness of the surface film. In order to obtain the optical constants of PbSe films laid on steel dispersion analysis was used. The dispersion analysis offers the advantage of processing a large volume of data. The RefFIT program was used for the dispersion analysis of the reflection-absorption spectrum of PbSe allows the spectra to be processed, which shows the interference fringes. In this case, the film thickness was used as an experimental variable parameter in fitting process.

Alias, M. F.A. et al., 2014, prepared thin films of Cu₃SnS₄ by chemical bath deposition (CBD) technique on glass substrate at 80 min deposition time and 1.5 pH four sample were prepared with different compositional ratio. The effect of substrate temperatures (313, 323, 333 and 343 K) toward the composition, optical properties and thickness of prepared thin films were investigated. The composition and optical properties of prepared thin films have been investigated by Rutherford back scattering and UV-VIS spectrophotometer respectively. The thickness of films ranged from 153.18 to 343.95 nm depended on substrate temperature and were calculated by weight method for all samples.

Thin Cu_3SnS_4 prepared at 313K substrate temperature and 1.5 pH (6S, whose standard moles formula as $Cu_4Sn_{1.12}$ $S_{2.88}$) has the lowest values in visible region for all optical constants, where direct energy gap (E_g^{direct}) was 2.5 eV with absorption coefficient > 10^4 cm⁻¹. The optical constants such as refractive index, extinction coefficient, real part of dielectric constant, and imaginary part of dielectric constant have values equal to (4.88, 0.175, 23.78, 1.71) respectively, while the optical conductivity has values greater than 10^{14} sec⁻¹, at wavelength 550 nm, therefore we find the sample 6S has new properties in visible region that can be used in photovoltaic devices.