GODFREY OKOYE UNIVERSITY

(The Catholic University of Enugu)

The Second Inaugural Lecture:

Thin Film in Solar Energy Technology

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Thin Film in Solar Energy Technology
Second Inaugural Lecture of Godfrey Okoye University, Enugu

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"Success is not final, failure is not fatal: it is the courage to continue that counts." **- Winston Churchill**

"I am a success today because i have friends who believed in me and i didn't have the heart to let them down"
- Abraham Lincoln

"The Concern For Man Himself And His Fate Must Always Form The Chief Interest Of All Technical Endeavours In Order That The Creations Of Our Mind Shall Be Blessings And Not A Curse To Mankind"
- Albert Einstein

Section 1:
Introduction

Energy keeps the world alive. It is an important index for evaluating a nation's status as per capita of electrical energy. Energy can be classified into renewable and non-renewable. Non-renewable energy comprises of fossil fuels which come in three principal forms from which many other products are derived such as coal, crude oil and natural gas. With the fossil energy crisis in view and some international policies about oil, scientist all over the world turn their attention to developing an alternative energy resources that will augment the conventional energy sources to meet the world energy demands. Apart from the depletion of fossil fuel, it has also been recognized that heavy reliance on fossil fuel has had an adverse impact on the environment. For example, gasoline engines and steam-turbine power plants that burn coal or natural gas send substantial amount of sulphur dioxide (SO_2) and nitrogen oxides (NO_2) into the atmosphere. When these gases combine with atmospheric water vapour, they form sulphuric and nitric acids, giving rise acidic precipitation which endangers plants and animals. Furthermore, the combustion of fossil fuels also releases carbon dioxide into the atmosphere; the amount of this gas in the atmosphere has been observed to have steadily risen since the mid-1800, largely as a result of the growing consumption of coal, oil and natural gas. More and more scientists believe that the atmospheric build-up of carbon dioxide (with that of other

industrial gases such as methane and chlorofluorocarbon) may induce greenhouse effect, causing rise in the surface temperature of the earth by increasing the amount of heat trapped in the lower atmosphere. This condition could bring about climate change with serious repercussions for natural and agricultural ecosystems. Renewable energy is inexhaustible as the material producing it is replenishable. Such renewable energy sources include Biomass, wind, marine, geothermal, oceanic/tidal, hydro-power and solar energy.

Basic concept of alternative energy sources relates to issues of sustainability, renewability and pollution reduction. Basic barrier to all forms of alternative energy lies in the initial cost.

The adoption of renewable energy technologies constitutes a win-win situation, as renewable is not only green and job generating, but also sustainable with more environmental benefits. Renewable fuels such as wind, solar, biomass, tides and geothermal are inexhaustible and free as a resource. They just need to be captured efficiently and transformed into electricity, hydrogen or clean transportation fuels. "Green energy" is a term used to describe the energy that is generated from the sources that are known to be non-polluting. It indirectly produces hydropower through the movement of rain water, biomass through photosynthesis and tidal power through tides caused by moon and sun. The green energy sources are environmental friendly and do not require environmental damaging, mining and transportation activities.

Renewable technology favours decentralization and more importantly attempts to seek local solutions to local problems. Therefore, the investment in green energy supply and progress should be encouraged by governments of all countries.

Let us discuss a little bit of one or two of these renewable energy sources:

I.   Biomass energy or bio-energy is energy from organic matter produced by anaerobic digester. The following wastes are used for such fuel production:

vegetable wastes from agriculture and forestry, vegetable wastes from food processing industry, fibrous vegetable wastes from pulp production and from production of paper from pulp if it is co-incinerated at the place of production and the heat generated is recovered, wood wastes with the exception of that which may contain halogenated organic components or heavy metals as a result of treatment with wood preservatives or coating and which includes wood wastes originating from construction and demolition wastes. And fumes from landfills can be considered as a biomass energy source'.

Biomass generates about the same amount of CO_2 as fossil fuels, but every time a new plant grows, CO_2 is removed from the atmosphere leading to the net emission of carbon dioxide to be zero as long as plants continue to be replenished for biomass energy purpose. The energy crops such as the fast growing trees and grasses, which are called biomass feed stocks, are the raw materials for producing bio-energy. The production of the biomass feed stocks can help increase profits for the agricultural industry (Nakicenovic et al., 1998)

This potential of ethanol fuel from sugarcane was demonstrated by Brazil in 1975. Within 1983 – 1989, majority of cars sold in Brazil consume neat ethanol. In addition, it created 700,000 jobs, farmers earned more and sugarcane farms and ethanol industries were established. $33 billion in oil imports was saved from the period 1976 – 1996. The ethanol fuel production has also improved urban air quality, reduced carbon emission, water pollution and soil degradation. Brazilian government was able to achieve this through giving low interest loans for the construction of distilleries and guaranteed purchase of ethanol by the oil companies with sales tax incentives. Nigeria on the other hand has the following possible locations: Papalanto and surrounding areas in Ogun State, Jebba and Bacita in Kwara State and the vast areas of Zaria, Yahuri in the Northern part of Nigeria for large scale production of sugarcane and setting up of ethanol production plants.

II. Solar energy is energy from the sun produced in the sun's thermonuclear reactor where two reactions- proton-proton and Bethe cycle reactions take place with helium molecule as the end product and radiated in different direction in the form of electromagnetic waves (sun rays) within spectrum of Ultraviolet (UV) of wavelength 0.3 -0.4μm, Visible of wavelength 0.4 – 0.74μm and Infrared (IR) of wavelength 0.74 – 4.0μm. The average amount of solar energy radiated to earth is about 1360 kW/m^2 depending on latitude and regional weather pattern (Green, 2001) and such parameters as: cloudiness index, clearness index, turbidity, albedo, transmittance, absorbance and reflectivity. Solar energy is very viable in Nigeria because her average sun hour is about 4.5 hours. However, the energy from the sun can be trapped directly as thermal energy using thermal collectors or directly to electricity (direct current) using photovoltaic cell (solar cells) arranged in arrays to form solar panels. The solar cells are made from semiconductors which act as non-conductor at room temperature and conductor above room temperature. Semiconductor could be single such as Silicon wafer or compound semiconductors (binary, Tennary, etc). Because of cost of solar panel due to high cost of silicon wafers, search for possible cheap alternative cells for the fabrication of solar panels using thin films is on the increase and that is why we have joined the numerous scientists undertaking research in thin film technology.

Section 2:

Thin Films and Properties

Thin films are crystalline or non-crystalline materials developed two dimensionally on a substrate's surface by physical or chemical methods. They play vital role in nearly all electronic and optical devices. They have been used as electroplated films for decoration and protection (Heaven, 1970). They have long been used as anti-reflection coatings on window glass, video screens, camera lenses and other optical devices. These films are less than 100 nm thick, made from dielectric transparent materials and have refractive indices less than that of the substrate (Pentia, et al, 2004). However, the use of techniques which have been developed over the last few years show that much of the thin films are of recent origin. Thin films of thickness less than 100 nm now serve as anti-reflection coatings on solar energy collectors. Thin semiconductor films on metal or glass substrate form a promising type of low cost solar cells.

In industrial, scientific and technical applications of thin films, their physical properties such as optical, chemical, electrical etc are investigated and the results are applied in several devices such as solar energy devices, xerography, switching devices, high resolution lithography, optic memories, photo-detectors etc.

Thin films deposition for optical, electronic and optoelectronic device application has become an industry in most advanced countries using highly technological, sophisticated and very expensive techniques. However, in the third world

countries, the high technological and sophisticated techniques are not easily achieved because of their complexity and the poverty of the third world countries. Hence, considerable efforts are put into developing simple and cheap techniques of depositing thin films. The solution growth technique offers the simplest, cheapest, most economical and affordable method of depositing thin films like Halide and Chalcogenide.

Benefits of Thin Films

Thin films could be used to produce solar panels which in turn, could be used to produce clean and quiet electricity. Such alternative source of cheap electricity will reduce electricity bills, guard against rising energy costs, protect the environment, add comfort, security and value to homes and provide uninterrupted power supply.

Since there are no moving parts, there is little or no breakdown in the provision of such systems. The systems have long life span. The solar panels themselves (the "engine of the system") are guaranteed for 20 – 30 years. There is virtually no maintenance on the panel. Distribution can be decentralized. It can be used to supply DC or also AC by using an inverter.

Many thin films have been developed for solar radiation absorption and glazing which are used for photo-thermal devices. However they are not yet fully developed for temperate and tropical environments to be used for heating and cooling in buildings. This could be due to lack of understanding of the need and prospects of selective glazing for buildings. There is also lack of interest due to the high cost of the films that have been developed for these applications.

Many scientists all over the world are now occupied with research into ways of improving the performance of solar energy devices to provide comfort in buildings and automobiles. The separation of the input solar radiation from the emitted thermal radiation by an absorbing material is needed in order to obtain

higher collector efficiency in this wise. A material which is capable of separating thermal (infrared) radiation from the input solar radiation is a spectral selective surface. Energy could be conserved, and an acceptable level of comfort is achieved inside buildings, when a suitable thin film is deposited directly onto the window glazing. This is referred to as solar control coatings or heat mirrors.

Solar control coatings are expected to play the role of a conventional air conditioner, but passive selecting only filters certain solar radiation that is required and screen of the infrared radiation (heat) from inside of buildings in warm climate. For solar control coatings, there must be controlled optical transmittance which ranges between 10-50% and low reflectance which is less than 10% in the visible region ($0.4\mu m$ – $0.7\mu m$) and high reflectance in the infrared region (> $0.7\mu m$). With this, there will be cooling of the inside of buildings as the infrared portion of the solar radiation which causes heating is screened off and there is also adequate illumination of the inside of the same buildings.

Optical and Solid State Properties of Thin Film
The optical and solid state properties studied in this work include: Absorbance (A), Transmittance (T), Reflectance (R), Absorption coefficient (α), Optical density (O.D). Others are the band gap, optical constants, refractive index (n) ,extinction coefficient (k), the dielectric constants- real (ε_r) and imaginary (ε_i), Optical conductivity (σ_o), dispersion and Electrical conductivity (σ_e).

Transmittance
The transmittance (T) of a specimen is defined (Wooten, 1972, Pankove, 1971, Lothian, 1958) as the ratio of the transmitted flux (I_t) to the incident flux (I_o) that is,

$$T = I_t/I_o \qquad\qquad (2.\,1)$$

Reflection at surfaces are usually taken into consideration, hence transmission is corrected for reflection and for scattering as well. With the corrections, the transmittance is called internal transmittance. If a specimen has a thickness d, an absorption coefficient, α and a reflectivity, R, the radiation reaching the first interface is $(1 - R)I_o$, the radiation reaching the second interface is $(1 - R) I_o \exp(-\alpha d)$ and only a fraction, $(1 - R)(1 - R)I_o \exp(-\alpha d)$ emerges. The portion internally reflected eventually comes out considerably attenuated. The end result is that overall transmission is given by (Lothian, 1958, Pankove, 1971, Wooten,1972) as:

$$T = I_t/I_o = (1 - R)^2 \exp(-\alpha d)/ (1 - R^2) \exp(-2\alpha d) \qquad (2.2)$$

Equation 2.2 accounts for the effect of multiple reflections in the film. When the product αd is large, the second term in the denominator becomes negligible and the transmittance is expressed according to (Lothian, 1958) as

$$T = I_t/I_o = (1 - R)^2 \exp(\alpha d) \qquad (2.3)$$

If R and d are known, equation 2.3 is used to solve for α. The measurements of the transmittance of two samples having different thickness d_1 and d_2 can also be used to solve for α using equation 2.4

$$T_1/T_2 = \exp[\alpha(d_2 - d_1)] \qquad (2.4)$$

Absorbance

The absorbance (A) is the fraction of radiation absorbed from the radiation that strikes the surface of the material. Alternatively, A is the logarithm to base 10 of the transmittance, i.e,

$$A = \log_{10} I_t/I_o = \log_{10} T \qquad (2.5)$$

It follows from equation 2.5 that the transmittance and absorbance are related by

$$T = 10^{A} \tag{2.6}$$

Hence knowing one, the other can be calculated. The absorbance (A) is determined directly from absorbance spectra measurements and the instrument scales are often calibrated in this unit (Lothian, 1958).

During the optical characterization of thin films, it is the spectral absorbance of the films that are obtained directly from the UV spectrophotometer thereafter, equation 2.6 is used to calculate transmittance. The other properties are obtained from calculations based on the above quantities (transmittance and absorbance).

Reflectance

This is the fraction of the incident radiation of a given wavelength that is reflected when it strikes a surface. A relation between transmittance (T), spectral absorbance (A) and spectral reflectance (R), according to the law of conservation of energy is given by

$$A + T + R = 1 \tag{2.7}$$

Equation 2.7 is used for calculating reflectance.

Absorption Coefficient

Absorption coefficient is the decrease in the intensity of a beam of photons or particles in its passage through a particular substance or medium. This is true when applied to electromagnetic radiation, atomic and subatomic particles. When radiation of intensity Io is incident on material of thickness d (μm) the transmitted intensity I_t is given by (Lothian, 1958, Pankove,1971) as:

$$I_t = I_o \exp (-\alpha d) \tag{2. 8}$$

For pure absorption, the constant (α) is the absorption coefficient. For scattering, obeying Bouguer-Beer's law, α is the scattering coefficient. For the total attenuation including both is the extinction coefficient given by the sum of the absorption and scattering coefficient.

$$T = I_t/I_o = \exp(-\alpha d) \tag{2.9}$$

and
$$\alpha = -[\ln T]/d \tag{2.10}$$

For a unit distance transversed, we have

$$\alpha = -[\ln T]/d \ (\mu m)^{-1} \tag{2.11}$$

$$\alpha = -[\ln T]/d \ \times 10^6 \ m^{-1} \tag{2.12}$$

Equation 2.12 is used to calculate the absorption coefficient in this work. For a selective transmitting surface, the selectivity merit is given as αT. This is the transmittance-absorptance product for the material.

Optical Density

The optical density (O.D) also called transmission density, is defined as the logarithm to base ten of the reciprocal of the transmittance.

$$\text{Optical density} = \log_{10} 1/T = \log_{10} I_o/I_t \tag{2.13}$$

In equation 2.2, the effects of multiple reflections taking place in the films is taken into account. We must know the value of R in order to evaluate α from equation 2.2. However, if R does not change appreciably in the frequency range of interest and using the approximation, $R^2 \exp(-2\alpha d) \ll 1$, the optical density as given by (Karlsson, et al. 2004). That is Optical density

$$(O.D) = \log_{10} [\exp (\alpha\, d) - 2 \log_{10} (1 - R)] \tag{2.14}$$

Hence,
$$\alpha = (O.D \times 2.303) /d - \{4.606 \log_{10} (1 - R)\} /d \tag{2.15}$$

At room temperature, R does not change by more than 2% in the wavelength range of the experiment (Myers, et al, 2002), hence, the second term in equation 2.15 is neglected and regarded as background because of its very slow variations. Equation 2.15 then becomes

$$\alpha = O.D. \times 2.303 /d \tag{2.16}$$

For the coated substrate used, that is glass, d is 1mm so that optical density is given as

$$O.D = \alpha \times 10^{-3} /2.303 \tag{2.17}$$

Band Gap and Absorption Edge

The band gap (E_g) is the energy needed to move a valence electron into conduction band. For a semiconductor it is the energy needed to free an electron from the nucleus of the parent atom. It is defined as

$$E_g = hf = 1.241/\lambda_o \text{ eV} \tag{2.18}$$

When an electron undergoes transitions from an upper part of the valence band to the lower part of the conduction band, it causes dispersion near the fundamental absorption edge and gives the shape of the absorption spectrum. This could happen without phonon participation and without a change in the crystal in which case, it is called direct transition. But when there is a change in the crystal momentum and interaction with phonon that changes electron energy, this is called indirect transition. Both direct and indirect transitions give

rise to different frequency dependency of the absorption coefficient near the fundamental absorption edge. The absorption coefficient for direct transition is given by (Moss,1961, Harbeke, 1972, McMahon, et al, 2002)

$$\alpha = (hf - E_g)^n \tag{2.19}$$

where h is Planck's constant and n = ½. If the transition between the upper part of the valence band to the lower part of the conduction band is allowed by the selection rules and n = 3/2, and if the transitions are forbidden, then

$$\alpha = (hf - E_g)^{1/2} \tag{2.20}$$

for allowed transitions and

$$\alpha^2 = (hf - E_g) \tag{2.21}$$

for forbidden transition, n = 2, E_g is the optical band gap. The indirect transitions give rise to

$$\alpha = (hf - E_g + E_p)^n \tag{2.22}$$

where E_p is the energy of a phonon with the required momentum.

Both phonon emission and phonon absorption are possible, where n = 2 and 3 for allowed and forbidden transitions, respectively. The dependence of absorption coefficient on the energy of light quanta corresponding to direct allowed transition is given by

$$\alpha = (hf - E_g)^{1/2} \tag{2.23}$$

$$\alpha^2 = (hf - E_g) \tag{2.24}$$

Thus a plot of α^2 against hf will give a curve with straight line at certain portion. However, at the region of its absorption edge, the absorption values fall to such a low value that the path due to band-to–band transition becomes difficult to measure. Experimental equipment or loses in specimen or other incidental absorptions are attributed to such low values (Moss, 1961) at the region of absorption edge. The plot of α^2 against hf in this region deviates from being straight. Extrapolation of the straight portion of the graph to point of $\alpha^2 = 0$ gives the energy band gap, E_g. The plot obeys accurately an exponential dependence on photon energy (Pentia, et al, 2004).

$$\alpha = \alpha_o \exp [-\beta (E_o - hf)] \tag{2.25}$$

where α_o denotes the cofactors placed before the exponent. E_o is energy comparable to E_g and β is a constant (at room temperature) having values in the range of 10 to 20 $(eV)^{-1}$. Some crystalline solids, notably alkali halides, show Urbach dependence given by $\beta = 0.8 /K_\beta T$ where β is temperature dependent near 300K, where K_β is the Boltzmann constant, T is temperature.

The minimum photon energy required to excite an electron from the valence to the conduction band is given by

$$hf = E_g - E_p, \tag{2.26}$$

where E_p is the energy of an absorbed phonon with the required momentum. For a transition involving phonon absorption, the absorption coefficient is given by

$$\alpha_a hf = B (hf - E_g + E_p)^2 / \exp (E_p/ K_\beta T)^{-1} \tag{2.27}$$

and for a transition involving phonon emission
$$\alpha_e hf = B (hf - E_g - E_p)^2 /(1- \exp (E_p/ K_\beta T)^{-1} \tag{2.28}$$

Since both phonon emission and phonon absorption, are possible for $hf > (E_g - E_p)$, the absorption coefficient is then

$$\alpha\, hf = \alpha_a\, hf + \alpha_e\, hf \qquad\qquad (2.29)$$

For many amorphous semiconductors, the energy dependence of absorption is experimentally of the form (Seraphin, et al, 1976, Elliot, 1984,)

$$(\alpha\, hf)^{1/2} = \alpha\,(hf - E_g) \qquad\qquad (2.30)$$

$$(\alpha\, hf) = B(hf - E_g)^2 \qquad\qquad (2.31)$$

where B is a constant which can be defined as

$$B = 4\lambda\sigma_o / ncE_e \qquad\qquad (2.32)$$

where c is the velocity of light, n is the refractive index, σ_o is the extrapolated conductivity at $1/T = 0$ and E_e is interpreted as the width of the tail of localized states in the band gap. The reciprocal of the constant B i.e. (B^{-1}) is called the disorder potential in the mobility gap of the amorphous semiconductor. This is obtained from the gradient of the graph of $\alpha^{1/2}$ against the photon energy (hf).

Absorption Edge
The absorption edge is caused by transition from the top of valence band to the bottom of the conduction band as discussed above. The energy band gap E_g is determined from the absorption spectrum by extrapolation to zero absorptance known as the absorption edge. It is noted that for transitions, the photon energy (hf) must be equal to or greater than the energy gap E_g (Omar, 1975), that is,

$$E_g \leq hf \qquad\qquad (2.33)$$

where f is the transition frequency

$$E_g = hf = hc/\lambda \tag{2.34}$$

where h is the Planck's constant = 6.62×10^{-34} JS
c is the velocity of light = 3×10^8 ms^{-1}, λ is the wavelength in metres (m).
Since 1J = 1.6×10^{-19} eV
Substituting into equation 2.34 gives
hf (j) = $(6.62 \times 10^{-34} \times 3 \times 10^8) / \lambda(m)$
hf (eV) = $6.62 \times 10^{-34} \times 3 \times 10^8 / \lambda(m) \times 1.6 \times 10^{-19}$
= $6.62 \times 10^{-34} \times 3 \times 10^8 / \lambda(\mu m) \times 10^{-6} \times 1.6 \times 10^{-19}$
hf (eV) = $1.241 / \lambda(\mu m)$ \hfill (2.35)

Equation 2.35 is used to calculate the photon energies in eV for various wavelengths λ in μm. At the absorption edge, equation 2.34 strictly becomes

$$E_g = hf_o \tag{2.36}$$
or
$$E_g = hc/\lambda_o \tag{2.37}$$

where λ_o is the minimum wavelength at the absorption edge. Equation 2.24 can be used to calculate the absorption edge.

The absorption edge for ZnS has been studied by Oladeji, et al. (1999), Ezema, (2003), Ndukwe, (1996) while Ezema, (2003) studied that of BeBr$_2$. The plot of log α against hf is a straight line within a wide range of temperatures (116 – 620K) according to these researchers. The absorption edge for CdS and CdSe were reported by Osuji, et al, (1998). Few compounds, Kale et al (2004) showed that the density of impurities affected the position of the absorption edge in such a way as to shift it towards much shorter wavelength. The effect of this is to cause a large increase in the band gap.

Optical Constants

The optical constants are the index of refraction (n) and the extinction coefficient (k). The discussions on optical constants are available in the literature (Heavens, 1955, Lothian, 1958, Pankove, 1971). The optical constants of a thin film material are most commonly and reliably determined from the simultaneous measurement of transmittance and reflectance of the film.

If a specimen has a thickness d, an absorption coefficient α and reflectance R, the transmittance is given by equation 2.9. The boundary between vacuum (or air) and an absorbing layer specified by refractive index (n), the extinction coefficient (k) and thickness (d) at normal incidence, yields the reflectance in terms of the optical constants of layer as

$$R = (n – 1)^2 + k^2 /(n + 1)^2 + k^2 \qquad (2.38)$$

For semiconductors and insulators, or materials in the range of frequencies in which absorption is weak, $k^2 << (n – 1)^2$ equation 2.38 reduces to

$$R = (n-1)^2 /(n+1)^2 \quad [21,22] \qquad (2.39)$$

Hence

$$n = (1 + \sqrt{R})/(1 - \sqrt{R}) \qquad (2.40)$$

Therefore, to determine n for any particular wavelength, the reflectance at that wavelength is determined for normal incidence only and n can be calculated. The absorption coefficient (α) can be defined with reference to extinction coefficient (k) by (Coutts, et al, 2001, Mahrov, et al, 2004) as

$$\alpha = 4\Pi k/ \lambda \qquad (2.41)$$

$$k = \alpha \lambda/ 4\Pi \qquad (2.42)$$

where k is called the extinction coefficient (k) or attenuation constant and it can be calculated.

Dielectric Constant

A dielectric is actually an insulator (or poor conductor of electricity). This affects how light moves, through materials. A high value of dielectric constant makes the distance inside the material look longer so that the light travels slowly. It also 'scrunches up' the waves to behave as if the signal had a shorter wavelength. For use in capacitor, it must be high and low in semiconductors for high speed signal to take place. The dielectric constant is given by (Wooten, 1972, Mahrov, et al, 2004) :

$$\varepsilon = \varepsilon_r + \varepsilon_I \tag{2.43}$$

$$\varepsilon = (n + ik)^2 \tag{2.44}$$

where ε_r and ε_i are the real and imaginary parts respectively of ε and (n+ik) is the complex refractive index. Hence,

$$\varepsilon_r = n^2 - k^2 \tag{2.45}$$

$$\varepsilon_i = 2ink \tag{2.46}$$

where n is the refractive index and k is extinction coefficient.

Optical Conductivity (σ_o)

Optical conductivity (σ_o) is the optical response of a transparent solid. It is given by (Wooten, 1972, Mahrov, et al, 2004) as

$$\sigma_o = \alpha\, nc\, / 4\Pi \tag{2.47}$$

where c is the velocity of light. Hence σ_o is the conductivity at the optical frequency concerned and is not generally equal to the direct current (DC) or low frequency conductivity. In metals, σ_o and k are very high as reflectance approaches unity. In semiconductors k is usually small, σ_o is reduced and reflectance is also reduced thereby giving higher transparency than in metals. In the case of insulators, k is very small

($k \to o$). The dielectric constant ε then tends to n^2 or $n \to \sqrt{\varepsilon}$.

Extinction Coefficient Factor

This is the product of absorption coefficient (α) and depth of penetration of radiation x. This is given by (El-Nahass, et al, 2003) as

$$F = \alpha x = \log\{(1-R^2)^2/2T + [R^2+(1-R^2)/2T]^{\frac{1}{2}}\} \tag{2.48}$$

Dispersion

Dispersion is the separation of a beam of white light into its coloured components thus producing spectra. Newton was the first to demonstrate dispersion using a glass prism. Dispersion has the following properties:

(i)   dispersion increases with decreasing wavelength.

(ii)   The refractive index increases with decreasing wavelength.

(iii)   For every material the higher the refractive index, the greater the dispersion.

(iv)   Every substance has its own shape of dispersion curve.

An empirical formula by Cauchy (Jenkins, et al,1976) is given by

$$n-1 = c_1 (1 + c_2/\lambda_2 + c_3/\lambda_3 +\text{---}) \tag{2.49}$$

where c_1, c_2 and c_3 are constants which are characteristic of any material. The quantity $n-1$ is called the refractivity for normal dispersion. Cauchy's formula hold satisfactorily. However, for a few materials, the dispersion deviates from the normal. Where refractive index increases with increasing wavelength over a narrow range of the spectrum, anomalous dispersion may result. A single oscillator model suggested by Sellemeier (Jenkins, et al, 1976, Born, et al, 1980, Green, 1981) is given by equation

$$n^2 - 1 = A_o \lambda_o /1 - (\lambda_o/\lambda) \tag{2.50}$$

where A_o and λ_o are the oscillator's strength and position, respectively. Thus, a plot of $1 / (n^2 -1)$ against $1/\lambda$ gives a slope of $1/A_o$ and an intercept of $1/A_o\lambda_o$. The refractive index of a semiconductor reaches a constant value at wavelengths significantly greater than that corresponding to a fundamental transition. Thus, semiconductors are often characterized by this undispersed value of the index of refraction n_o or by $(n_o)^2$ which is known as the high frequency dielectric constant.

Photoconductivity

Thermal excitations produce electronic conduction in solids. When photon energy is greater than the band gap of materials, excitation takes place. The interaction of a solid with light of appropriate wavelength creates electron-hole pairs. The phenomenon of photo-conductivity is therefore the increase in electrical conductivity of a solid when irradiated with light. The concentration of carriers in illuminated materials is in excess of their values in the dark. The excited carriers decay back to their equilibrium values when the light is switched off. Recombination is the process whereby the decay occurs. This may be radiative, in which an electron occupying a higher energy state makes transition to an empty lower energy state accompanied by the emission of light. Many semiconductors exhibit photo-conductivity and the phenomenon is the basis of many optoelectronic applications (Bube, 1976, Nair, et al, 1989).

Luminescence

Luminous efficiency is the emission of radiation (UV, VIS or IR) as a result of electronic excitation of a material which excludes any radiation that is of the temperature of the material. Luminescence refers to processes in which excited electrons decay into lower electron states thereby giving rise to emission of radiation. The electron excitation mechanism may be by means other than absorption of radiation and results in different forms of luminescence which include photo-luminescence, thermo-luminescence, electro-luminescence, cathode-luminescence and chemo-luminescence.

(i)   Photo-luminescence: This involves the excitation of electron by optical radiation. It can be used as optical shutters to high IR light (Mahrov, et al 2004).

(ii) Thermo-luminescence: This is the excitation by thermal energy. Thermo-luminescent materials can be used as chromogenic materials (Warner, et al, 2005).

(iii) Electro-luminescence: This is the excitation by electric current. It is the optical radiation obtained by injection of minority carriers across the region of a semiconductor p-n junction where radiative transition takes place.

(iv) Cathode-luminescence: This is the excitation by high energy electron beam.

(v)   Chemo-luminescence: This is the excitation by chemical reactions. Materials having this property can be used as chromogenic materials. In a decay process where a free electron in the conduction band recombines with a hole in the valence band and a photon is emitted, it is called band-to-band recombination of the electron and hole.

The recombination process occur in both direct gap and indirect gap semiconductors (Pankove,1971, Moss, *et al*, 1973). For a direct gap semiconductor, the energy spectrum of the emitted photons will have a low energy band gap. While for indirect gap semi-conductor, the band-to-band emission of photons with phonon participation is a three body process due to the requirement of conservation of energy and momentum. The probability of indirect recombination is smaller than that of direct electron–hole. Recombination of electrons and holes in semiconductor generally results in emission of photon energies above a low energy band gap.

Electrical Conductivity
The electrical properties of a selective thin film can be measured. The following standard equipment and methods are used for measuring resistivity and conductivity of the materials: the electrical bridge, four point probe, the Hall effect, electronic instrumentations such as a digital multiplier etc. Another method is to deduce these values from optical properties. The electrical

conductivity is deduced (Blatt,1968, Suchet, 1976,   Cox, 1987) using the equation

$$\sigma_e = E_c^2/\omega = E_c^2/2\Pi f = E_c^2 \lambda/2\Pi C \tag{2.51}$$

where E_c is wave number and ω is the angular frequency or

$$\sigma_e = 2\lambda_o\sigma_o /\alpha = 2\lambda\alpha nC /\alpha 4\Pi = \lambda nC /2\Pi \tag{2.52}$$

$$\sigma_e = 2\Pi E_c\omega\varepsilon. \tag{2.53}$$

Thermal Conductivity

The thermal conductivity σ_T of any material is related to its electrical conductivity by the equation (Berman, 1976)

$$\sigma_T / \sigma_e = \Pi^2 /3(K_\beta/e)^2 T \tag{2.54}$$

where K_β is the Boltzmann constant, e is electronic charge, T is absolute temperature. The coefficient at the right hand side (RHS) is a constant

$$\sigma_T / \sigma_e = \text{constant} \times T \tag{2.55}$$

This is known as Weidmann –Frank-Lorentz law. Thermal conductivity can be written as

$$\sigma_T = \sigma_e T \times \text{constant} \tag{2.56}$$

$$\sigma_T = \sigma_e \Pi^2 /3 (K_\beta/e)^2 T \tag{2.57}$$

A selective absorber is required to have high conductivity. Heat mirrors should have low thermal conductivity while cold mirrors should have high thermal conductivity so as to conduct heat away and remain a cool surface.

Section 3:

Application of Thin Films

One prominent application of these optical properties is manifested in the phenomenon in which some surfaces can be modified to absorb, reflect and transmit light.

Spectral Selective Surfaces Aspect of Solar Energy Application

For many important solar energy applications, one can achieve some degree of energy efficiency by using surface with spectral selectivity. By spectral selectivity of a material medium, it is meant that the radiative properties such as transmittance (T), absorbance (A), reflectance (R), and emittance, (ε) of the material have different values at different parts of the electromagnetic spectrum of solar radiation. This phenomenon, that is, spectral selectivity is often achieved by the use of coatings onto substrates, which may be transparent or opaque depending upon the thickness of the deposit.

In the determination of the efficiency of solar conversion processes, for example, materials and coating play important role. Optical materials and those produced by coatings include selective absorbers, heat mirrors, reflective materials, anti-reflective materials and fluorescent concentrator materials. Others are holographic films, cold mirrors, radioactive cooling surfaces, optical switching films and transparent insulating materials. The efficiency of photovoltaic, energy efficient windows and many hybrid designs are improved by the use of the above materials and spectral selective surfaces.

Spectral Selectivity

The incident solar radiation on the surface of material medium, for example a photo-thermal converter device, is subjected to several processes. The processes are dependent upon the optical properties of the surface intercepting solar radiation. The interaction of the electromagnetic fields of the solar radiation with the electric charges of the material, results in the modifications of solar radiations at some parts of the solar spectrum. The modifications include some parts being absorbed and transformed into heat, some being transmitted through the material and some are reflected back to space or into an enclosure (Granquist, 1985, Lovel, et al, 1976).

The optical effects arising with the interaction of a surface with solar radiation differ with different materials. Whenever the optical properties of a material surface vary with wavelength referred to as spectrally "selective". This phenomenon is known as "spectral selectivity". Spectral selective surfaces are therefore surfaces whose absorbance, emittance, transmittance and reflectance with respect to radiation are wavelength dependent and vary over the spectral region of 0.3μm to 3μm which is the wavelength range of solar radiation (Lovel, et al, 1976, Meinel, et al, 1976). The different thermal infrared radiation absorbed by a material or environment from the incident solar radiation, to achieve a desire effect, spectral selectivity is used (Meinel, *et al*, 1976, Granquist, 1985).

Solar Selective Absorber Surfaces

When solar radiation falls on a solar collector device, it is absorbed. The radiation absorbed is converted to thermal energy and is delivered to a heat transfer medium. If, therefore, solar radiation is incident on materials that absorb mostly at the short wavelength region, that is, $0.2 \leq \lambda \leq 3\mu m$, thermal radiation at $\lambda > 3\mu m$, component is either transmitted or reflected and spectral selectivity takes place. Spectral selectivity, in this case is the high absorbance and low reflectance in the $0.3\mu m < \lambda < 3\mu m$ wavelengths range, and low

absorbance and high reflectance at 3μm < λ < 100μm this makes available a reasonable proportion of heat for useful work depending upon the percentage of this in the solar radiation spectrum. A good solar absorber has the absorption edge at about 2μm. Its coatings may be homogeneous or have particulate structure. Several researchers (Nieminen et al, 2001, Chen,et al, 2003, Ezema, 2004, Ezema, et al, 2003, Mitsuaki, et al, 2003, Ezema, 2004, Shwarsctein, et al, 2006, Ezema, 2005, Ezema, 2005, Ramanathan, et al, 2003) have reported metal oxides on metal substrates which show desirable properties for solar collectors. Lead sulphide coatings, for example, were studied by (Reddy, et al, 1987, Bode,1996, Thangaraju et al, 2000). They concluded that the particulate structure affected the selectivity significantly.

Conditions that should be met by selective surfaces include:

(i) suitable environmental conditions e.g. temperature;

(ii) they should have a proper spectral profile that is high in absorbance or emittance but low in reflectance or transmittance within the wavelength range of 0.3μm to 3μm. This implies that such a surface appears black in the short wavelength range and becomes an excellent mirror in the thermal region;

(iii) must have long life span.

Semiconductor- Metal Tandems

These are called absorber – reflector tandems. When two materials combine to form a single device, they are referred to as being in tandem. One part is a semiconductor of a band gap of 0.6eV, which reflects in the wavelength region λ < 3μm. The other component is a metal that absorbs in the wavelength region λ > 3μm. Two basic systems or devices are obtained in semiconductor- metal tandem. If the reflector intercepts sunlight first, then the infrared components are reflected. In this case, the system is a "heat mirror". This is applied especially in transparent insulation for architectural windows (Lampert, 1985). If the absorber intercepts sunlight first, it absorbs the IR component and reflects or transmits the short waves component. The system then acts as a "dark mirror". This is the system used in most photo-thermal converters.

Heat Mirrors

A heat mirror, also called a transmitting selective surface, transmits in UV-VIS region and has a high reflectance in the IR. Heat mirrors are used to reduce the temperature in buildings. In the heat mirror, the reflector layer covers the non-selective absorber base. In this way, the selective reflector reflects in the thermal infrared > 3µm and transmits in the solar range < 3µm, so that the short wave components of the solar radiation are absorbed by the black absorber. Some highly doped semiconductors such as InO_2, SnO_2 or the mixture of the two, that is Indium-Tin-Oxide (ITO) have served well to produce this device (Seraphin, 1979). The ITO films are suitable up to temperatures in excess of 300°C. They adhere well to glass, resist chemical and environmental attack. A simple design utilizing a heat mirror can be used to separate heat and light from the solar spectrum. The IR energy could be used for thermal purpose and the high energy visible wavelength range could be used for a photovoltaic purpose (Lampert, 1985).

Dark Mirrors

In the dark mirror, the absorber is spectrally selective. It absorbs in the solar range λ < 3µm and transmits in the thermal infrared λ > 3µm. The surface of the absorber facing the sun must be of low reflectance in the short wave to let the solar photons penetrate. Several semiconductors have been used on different base materials e.g. silicon on silver, germanium on silver (Seraphin, 1974), lead sulphide on aluminium (Bode, 1996).

Anti-reflection Coatings

Reflection occurs each time electromagnetic radiation passes from one medium to another. Reflection losses, which can be disadvantageous in solar collector glazing, are caused by optical interference from the boundary formed between different media. As the propagating electromagnetic wave passes from one medium to another there is a change in phase velocity, wavelength and direction. Because of the interaction between the incident wave and the atoms of the new

medium, a reflected wave is propagated (Lampert, 1985). The deposition of anti-reflection coatings increases the transmission of light in optical lens systems and also increases the contrast by eliminating ghost images and reducing of stray light.

Anti-reflection reduces reflections thus resulting in improving the transmission of the glass. The special double layers created can also be used for reducing the reflection of temperature- sensitive optical components made of inorganic glass. Such a coating of inorganic films on organic glasses improves the mechanical durability. The coating system is very resistant to climatic effects, humidity, salt, water, organic solvents and cleaning agents. Anti-reflection coatings make up the majority of all optical coatings produced. They are used for example on lenses of photographic objectives, on ophthalmic glasses, on the lenses and prisms of binoculars, microscopes, range finders, periscopes, on instrument cover glasses and on sights and the modern high speed objectives in photography.

Spectral Splitting and Cold Mirror Coatings

Spectral splitting coatings are used to divide solar spectrum into various broad band regions and by so doing various regions can be used, in particular, for photovoltaic or photo-thermal needs (Lampert, 1985). A cold mirror has opposite spectral response to that of the heat mirror. Cold mirror films reflect highly (low transmittance) in the VIS region of electromagnetic (E.M) spectrum but reflect poorly in the IR region. The high energy light is used for photovoltaic generation while low energy light (IR) is used for photo-thermal heating of fluids. The separation of high energy IR light from low energy due to coatings are useful in thermal systems. They can be used in a greenhouse with some special arrangement of baffles (partitions) on the roofs. They reflect the photosynthetic active radiation (PAR) = $0.35\mu m$ to $0.75\mu m$ into the green house while transmitting the IR into the air channels which can be managed properly to maintain a suitable temperature in the green house. ZnS/MgF_2 and TiO_2/SiO_2 are material systems that have been devised for this purpose.

Radiative Cooling Materials

By radiative transfer of thermal radiation through windows in the atmosphere, the earth is naturally cooled. This happens mostly in the night. This natural window allows transmission of thermal radiation of 8μm < λ < 13μm region of the electromagnetic spectrum back to space.

Window Coatings

It is a micro thin layer of polyester, with a durable clear scratch resistant coating, that is professionally installed on clear or tinted glass. It provides a retrofit solution to many glass related problems such as excessive heat build up, harsh glare, UV damage and also providing safety, security and privacy.

The selective window coatings (Granqvist, et al, 1991) consist of two groups, those with static properties and those with dynamic properties. Window coatings with external optical performance factors are said to have static properties (Chopra, et al, 1983, Lampert, 1985,). This group is subdivided into two coatings which are solar controlled and low thermal emittance. The second group has dynamic properties and encompasses optical switching coatings of different types.

Solar Control Coatings

In hot climates, solar radiation entering through the windows is absorbed in the room and causes heating. To achieve comfortable temperature indoors, solar control coating surfaces that are transparent in the range 0.4μm < λ < 0.7μm and reflecting in the range 0.7μm < λ < 3μm are used. This means that the infrared part of the solar radiation is reflected. It is possible through the use of solar control windows to achieve a 50% reduction in the transmission of visible light. The use of such windows may achieve the same objective as the conventional air conditioner in the building. Such windows will be found most useful in hot climates such as the tropical region like Nigeria.

Low Thermal Transmittance

When a medium is generally opaque to the passage of radiation and selectively transmits a particular small range of radiation, it is said to operate as a window in that range. The low thermal transmittance window reduces the heat radiation through the window. To achieve low thermal transmittance window, surface coatings that transmit within $0.3\mu m < \lambda < 3\mu m$ and reflect within $3\mu m < \lambda < 100\mu m$ can be used. This means that maximum use is made of the solar energy in the short wavelength range while the transmittance of thermal radiation is minimized.

Materials for Solar Control and Low Thermal Transmittance

A thin homogeneous metal film can combine transmission in short wavelength up to about 50% as well as high reflectance in long wavelength (Theye, 1985, Chakrabarti, et al, 2004). The required thickness in the case of copper, silver and gold is about 20nm. If the films are thinner than this , they are not useful as they tend to break up into discrete islands and have strong absorptance of the visible light. Enhancement of luminous transmittance to more than 80% without significantly impairing the low thermal emittance can be achieved by embedding the metal in an anti-reflecting dielectric with high refractive index layers such as TiO_2. For a three layer coating, the thickness of the components can be tailored to meet the requirement of warm and cold climates. We have as an alternative to the metal based coatings the doped oxide semiconductor coatings. A wide band gap is needed in the semiconductor to permit high transmittance in the luminous and solar spectral ranges. To make the material metallic, electrically conducting and infrared reflecting for wavelengths exceeding a certain plasma wavelength, it must allow doping to a significantly high level. The semiconductors that are able to combine these properties are oxides based on zinc, cadmium, tin, lead and thallium and alloys of these. The doping is often achieved by the addition of some foreign element. Improved optical and electrical properties have been obtained with magnesium cadmium sulphide (Ezema, et al 2006), cadmium sulphide (Metin, et al, 2003, Rusu, et al, 2004) and TCO (Oladeji, et al, 2000), cadmium

zinc sulphide (Song, et al, 2005) and zinc cadmium sulphide (Salem, 2002). However they are toxic. This imposes a limitation on their large scale window production. The excellent chemical and mechanical stability of the doped oxide semiconductor has a specific important advantage.

Window Coatings with Dynamic Properties

Solar control and low thermal transmittance coatings are limited by ambient conditions. This is a disadvantage to an extent. A good window coating with dynamic properties, also known as a "smart window", is observed to be a better alternative. Smart coating (smart window) is a structured coating systems that provides for a double glazed window made possible by coating the outer pane. The incident solar radiation flooding the buildings can be regulated through various physical processes. The energy efficient window coatings with dynamic properties are optical switching coatings. This means that when there is variation in the external conditions, there is a switch of optical properties. In other words, it offers radical change in light intensity, spectral composition, heat, electrical field or injected charge. This optical change is manifested in transformation from highly transmitting to reflecting, either totally or partly over the solar spectrum. The purpose of such a device would be to control the flow of light and / or heat into and out of a window of a building. This device also could control lighting and heating levels for energy load functions. Three kinds of such devices exist in this group. They are the photo-chromic, thermo-chromic and electro-chromic coatings. These have been fully described in the literature (Seraphin, 1979, Lampert, 1985).

Section 4

Methods for Thin Film Growth

There are several ways of preparing halide and chalcogenide films. Preparation techniques and method of producing these films range from very simple and cheap to complex and very expensive ones depending on the substrate coating materials and on the required performance of the films (Chopra, 1969, Quijada, et al, 1998,). The methods for depositing thin films may be broadly classified under two headings: physical and chemical techniques. The physical techniques which are the broad categories of physical vapour deposition (PVD), sputtering techniques, plasma techniques etc. The chemical techniques which are chemical vapour deposition (CVD), spray pyrolysis, electrochemical deposition (ECD), anodization, spin coating, dip coating, solution growth technique (SGT) etc.

Chemical techniques are simple, cost effective and offer large area of uniform and controlled deposition for the preparation of halide and chalcogenide films. The growth technique is the simplest and the cheapest chemical technique. In all these techniques, three basic steps are followed in the formation of films. These steps are:
- creation of the species required for film formation, the transport of these species through a medium, and
- finally the condensation of the species on the substrate and subsequent coalescence to form the film.

Thermal Evaporation
Vacuum evaporation is the easiest to understand and is possibly the most widely used method for the preparation of thin films. The starting material is vaporized

or sublimed into gaseous state and the atoms (molecules) from the evaporation source are collected on to the substrate. The deposited species finally re-arrange or modify their bonding on the surface of the substrate. In practice, the evaporation is carried out in vacuum to reduce contamination. The production of base pressure, typically of the order of 10^{-6} torr in the chamber, is done by oil diffusion pump together with the nitrogen cooled trap. The nitrogen cooled trap is used to eliminate water vapour and to a lesser extent hydrocarbon contamination. The evaporant is placed on a source whose temperature is raised. The evaporant source takes different form. A boat containing a powder material acts as a resistance element between two electrodes for the passage of large DC current. The boat materials are made of high melting point metals, e.g. Mo or W, which are usually employed for the deposition of low melting point compounds. When it comes to high melting point compounds, the vaporization of the sample is done by bombardment with high energy electrons from an electron gun placed in the chamber. This makes it possible to heat the sample to its melting point.

The rate of free evaporation, in vacuum, of atoms from a clean surface of unit area is governed by the Langmur Dushman kinectic theory equation (Chopra, 1969).

$$N_e = 3.513 \times 10^{22} \, P_e \, \sqrt{(MT)^{-1}} \text{ molecule/cm}^{-2} \text{ s}^{-1} \tag{4.1}$$

where N_e is the number of molecules evaporated from the unit area per second, P_e is the equilibrium vapour pressure (in torr) of the evaporated material under saturated vapour conditions at a temperature T and m is the molecular weight of the vapour species.

However, the rate of deposition of the vapour on the substrate depends on the surface geometry, its position relative to the substrate and the condensation coefficient. A uniformly emitting point source is known as a Knudsen effusion cell. For such a source emitting onto a plate substrate, the rate of deposition follows Knudsen cosine law,

$Cos\theta$ /r². In the case of evaporation from a small area onto a parallel plane substrate, the rate of deposition is proportional to $Cos\theta$ /r². In both cases r is the radial distance between the source and the substrate, and θ is the angle between radial vector and the normal to the substrate direction. Deposition rate and thickness can be controlled by various systems:

   (i)   by making use of quartz crystal that changes frequently with change in film thickness on the face of the substrate,

   (ii)   by the use of ionization gauge- this measures the excess ion current due to the presence of the evaporant,

   (iii)   by employing mechanical arrangement that deflects due to impingement of the vapour species or as a result of the weight of the film. Multi-component films can be obtained by means of evaporation from two or more sources (Gunder, 1966, Young, et al, 2002). The establishment of equilibrium is prevented in convectional thermal evaporation because the vapour is removed immediately from the vicinity of the molten source. This leads to elements with the highest vapour present in the source alloy, to evaporate first thereby depleting the source and leading to compositional in-homogeneities in the deposited film. In order to remedy the situation, use of flash evaporation is made (Coutts, 2002, Kijatkina, et al, 2003, Lee, et al, 2003). In flash evaporation, powdered material is dropped steadily onto a heated ribbon, thereby almost instantaneously evaporating it. A further complication may arise in both flash and convectional evaporation that the dominant (equilibrium) vapour species may not have the same composition as the source material (Coutts, 2002).

Apart from the resistive (Huang, et al, 1982, Pawar, et al, 1986,) and radio frequency heating (Ibrahim, 1995) method, other forms of thermal evaporation exist depending on the nature of the evaporant. These include arc evaporation (Bhattacharya, et al, 1983, Rai, 1993), which is mainly for refractory metals such as W, Nb, Ta and Mo, exploding wire technique (Rodrigo, et al, 2002, Raghupathi,

et al, 2005,) and laser evaporation (Nair, et al, 1987). The principal demerit of thermal evaporation as a deposition technique lies in the variability in purity and composition of the resulting films in the case of alloys. Several factors combine to produce this variability. These include:

- (i)   substrate temperature,
- (ii)   substrate- source separation and orientation,
- (iii)   base gas pressure in the chamber,
- (iv)   impurities from the evaporation boat or desorbed gases from the surfaces,
- (v)   boat or filament temperature. Several materials (Si, Ge, GaAs, As_2Se_3, SiI_2, PbS, ZnS, CdS, CdSe etc) have been prepared by these techniques.

Epitaxial Growth

Epitaxy is the technique whereby oriented growth of a film can be achieved (Froment, et al, 1995, Osuji, 2003, Tatsumi, et al, 2004). It denotes formation of mono-crystalline films, usually on mono-crystalline substrate, either of the same substance, which is referred to as homo-epitaxy, or of other substances, which is termed hetero-epitaxy. The aim of a well oriented growth is to achieve a well ordered single crystal state or large oriented grains or mosaic mono-crystals which is required for solar cells application. The formation of regularly oriented reaction layers growing upon a substrate by chemical reaction between the basic materials and a substrate which may be a solid, liquid or gas is called chemoepitaxy. The oriented growth on amorphous specially shaped substrates is termed graphoepitaxy. The cause of epitaxy is not simple since it can occur between materials of different crystal structure and of different chemical bonding.

In hetero-epitaxy, the binding forces in the substrate are in general, different from those in the film. These binding forces determine the band structures and consequently the physical and chemical properties. The substrate temperature is

a fundamental parameter of epitaxy growth. There is a certain critical epitaxial temperature for every pair of materials. Above this, epitaxy is perfect while below this, epitaxy is imperfect or does not exist. For a given pair of materials, the epitaxial temperature depends on the rate of evaporation. Deposition rate R is another significant factor for epitaxy. R is given by

$$R = A \exp (Q_d /K_\beta T_e) \tag{4.2}$$

Where A is a constant, Q_d is the activation energy of surface diffusion, K_β is the Boltzmann constant and T_e is the epitaxial temperature. Equation 4.2 prescribes that an atom must have enough time to jump into a position of equilibrium before it collides with another atom. It is only at low deposition rates that epitaxy is formed. At higher rates, crystal twins are formed. Contamination which may be caused by an adsorption of residual gas especially at the higher working pressures influences epiaxial growth. Epitaxial temperature may rise or fall depending on how the adsorbed substance affects the mobility of atoms over the substrate.

Molecular Beam Epitaxy (MBE)

Molecular beam epitaxy is needed when epitaxial films of extreme purity with almost ideal crystal structure are needed. The physical principle of the MBE technique is the same as for classical evaporation. The differences include: very good vacuum conditions preserved during the whole process, precise in situ measurements of all important parameters of the films, and automatic control of the whole set up. The MBE (Oladeji, et al, 2000, Ezekoye, et al, 2003) is a type of expitaxial growth in which the films were grown by the condensation of one or more directed beams of atoms and/or molecules from a Knudsen effusion source under ultra-high vacuum conditions. A crucible heated by radiation of a heater is shielded by one or two thermal shields and its temperature measured by a thermocouple. The source is made up of a metallic chamber with a small orifice, so that a virtually saturated vapour pressure is maintained inside the crucible. This pressure depends explicitly on the temperature of the Knudsen cell. Several

Knudsen cells are placed as evaporation source for different substances, each cell having its own automatically controlled shutter that enables the determination of the thickness of the deposited film. To ensure prevention of pressure increase during evaporation, all sources are placed inside a cryopanel cooled by liquid nitrogen. This also ensures condensation of gases liberated from the source and surrounding. A mass spectrometer connected through feedback to heaters of a particular cell controls the evaporation rate from a particular film. The reflecting high energy election diffraction (RHEED) simultaneously checks the crystal structure. It is possible to incorporate an automatic device to stop the process, if the structure begins to be imperfect. The whole chamber works in ultra-high vacuum with many accessories, such as the AES, SEM, SIMS etc. included in the equipment for monitoring and control of the deposition and growth conditions.

The whole set up is computer controlled and moreover, it is possible to predict by means of a corresponding program, the properties of the sample produced (composition, thickness, number of layers). The fabrications of complicated layered multi-component structures which are not attainable with other methods are possible. However, because of the complexity of the system and its high cost, not many laboratories can afford this system. Several advantages are offered by MBE to the silicon device industry. The first is the capability of growing new structure which could not otherwise be fabricated. The second is improved dopant control. Secondly, the profile resolution in a single growth process to replace the multiple processes for complex devices. The third is that new material combinations are possible with a low growth temperature and a high purity ultra-high vacuum environment.

Liquid Phase Epitaxy (LPE)

It is a growth based on crystallization of semi-conducting materials dissolved in a suitable metal and is used to deposit semi-conducting epitaxy films. Metals with low temperature melting point are usually used (eg. Sn, In, Pb, Bi, Ga.) At a high temperature of about 1000℃, a saturated solution is prepared and then gradually cooled. A crystalline phase begins to flow over a given substrate when

the solution is supersaturated. By chemical or mechanical means, the solution is removed from the substrate. The LPE has been used to prepare good quality IIIA-VA compounds (Quijada, et al, 1998).

Sputtering

Although thermal evaporation is complicated, the sputtering technique is rather more complicated but enjoys the advantage of being far more flexible. Sputtering is the ejection of atoms from the surface of a material by means of the bombardment of surface with energetic particles. It consists basically of the bombardment of a target by emergent ions from a low pressure plasma causing erosion of material either atom- by – atom or as cluster of atoms and subsequent deposition of a film on a substrate (Maissel, 1966, Cruz-Vazquez, et al, 2001). The application of a high negative voltage to a target surface is the simplest way of inducing sputtering. This attracts positive ions from plasma. This is the case for DC sputtering process used for targets that are composed of metals, or at least consisting of materials sufficiently electrically conducting that the target can act as an electrode. When the sputtering chamber containing the required gas, usually Ar, is maintained at a residual pressure of about 10^{-2} torr, a high voltage DC(1-3KV) between cathode and anode, and a series of resistance of 1-10KΩ, the charges are accelerated towards the cathode where they bombard the target material to eject the surface electrons. The ejected atoms traverse the medium and are deposited at the substrate on condensation. A more common approach is to apply rf field (at typically 13MHz) to the target. For a target, both metallic and insulating material may be used. The rf voltage is capacitively coupled to the target surface by connecting a capacitor in series with the metallic targets. In the case of insulating surface, they are bonded usually to a metallic backing electrode which itself acts as a capacitive component.

A residual pressure of less than 10^{-6} torr is needed at the sputtering chamber. The sputtering inert gas used is Argon which is introduced at a higher pressure of about 1 to 20m torr. A plasma is struck when rf voltage is applied. During each

negative half cycle, positive ions are attracted to the target. More ions are attracted to the front surface of the target in the respective half cycles resulting in a build-up of a negative bias due to the mobility of electrons that is higher than that of ions in the plasma. After sometime, ions are attracted from the plasma essentially by the bias potential rather than the rf potential. The ejected material from the target is then carried to the substrate by the following half cycle of the rf fields. The relatively low temperature of the substrate ensures that crystallization was prevented, hence the deposited material can form an amorphous film if the atom mobility is sufficiently low. Homogeneous and uniformly thick samples are produced by this method.

The use of rf field in sputtering can produce amorphous samples of materials of interest. It is superior to evaporation method for the production of multi-component systems because the targets are already in compound form. This is because sputtering rates for different elements do not vary widely, unlike melting points, vapour pressures and therefore evaporation rates. As a consequence sputtered films tend to preserve the stoichiometry of the starting materials. Examples of rf sputtered films are CdZnS and metal modified ZnS/CdS (Cruz-Vazquez, et al, 2001, Oladeji, et al, 2005).

Further option offered by sputtering is the use of gases other than argon which chemically react with the target resulting in reactive sputtering. In this, the sputtering rate is increased significantly and helps incorporate chosen additives into the films. Sputtering has been used to produce hydro-generated amorphous silicon in an Ar-H_2 mixture. Also produced are doped amorphous silicon films in Ar : H_2 : N_2 /PH_3 mixture and amorphous transition- metal oxide material in Ar : O_2 mixture (Meinel, et al, 1076).

Factors which cause variations in the films produced by sputtering process include sputtering gas pressure, rf power applied to target, bias voltage of target or substrate and ratio of partial pressure of reactive sputtering. The factors which cause variation in the films produced by vacuum evaporation are also

significant in the sputtering (Glang, 1970, Vossen, et al, 1978   Eckertova, 1986,) such as magnetron sputtering, ion beam sputtering and discharge sputtering.

Chemical Vapour Deposition (CVD)

This is widely used in the preparation of thin amorphous and crystalline films of high purity. In this technique, condensation of compound from a gaseous phase was deposited onto a substrate (Vankar, 1985). It involves the exposure of the substrate to one or several vapourized compounds or reagent gases, some or all of which contain constituents of the desired deposited material. External means may be used in some cases to activate the chemical reaction. These include the application of an electric arc or glow discharge, rf field, light or x-ray, heat or electron bombardment etc. Several types of chemical reaction available are:

(a) Pyrolysis Reaction

In this reaction some compound in gaseous state can be made to suffer pyrolytic decomposition on a hot substrate to give a pure elemental deposit. This is useful in the decomposition of mainly metal halide, hydrides, carbonyls etc., depending on the operating temperature. Examples include (i) decomposition of pyrolytic graphite from methane (CH_4) which occurs at a substrate temperature of 2200°C (ii) decomposition of silicon from silane (SiH_4) which takes place in the temperature range of 800 - 1350°C and (iii) decomposition of nickel from the carbonyl form [$Ni(CO)_4$] which occurs at about 100°C.

(b) Reduction Reaction

Hydrogen reduction is essentially hydrogen assisted decomposition and is a commonly used reducing agent. Some examples are deposition of silicon by the hydrogen reduction of silicon tetrachloride which takes place at about 1000°C, and the decomposition of tungsten by the hydrogen reduction of tungsten hexafluoride which takes place at about 800°C. The reaction could introduce contamination in the deposited film as HCl may react with the deposited film or

even the reactor wall material. Reduction can also be achieved by a reaction of the type.

$$A + AB_2 \rightarrow 2\ AB \tag{4.3}$$

where AB is a gaseous compound, A is the substance to be deposited. The character of the reaction is such that at high temperatures the compound AB is stable, whereas at lower temperature the A component separates out. An example of the reaction is

$$2SiI_2(gel) ==== SiI_4\ (gel) + Si\ (solid) \tag{4.4}$$

where the reaction takes place at a temperature of 900℃

(c) Oxidation, Nitridation and carbidization

The reactions involve the reactions of gaseous ammonia (NH_3), methane (CH_4) and carbon dioxide (CO_2) with gaseous metal bearing compounds to form the nitrides, carbides and oxides respectively of the appropriate metals. For examples, silicon nitride films can be deposited by the reaction of silane with ammonia and titanium carbides at a substrate temperature of 1850℃.

(d) Chemical Transport Reactions

In the chemical transport reactions a relatively nonvolatile substance is transferred from the position of the source to the substrate position by means of a relatively very high volatile chemical vapour. The given substance is treated with HCl or other gas vapour to form the volatile compound which is transported to a substrate of suitable material, where it is deposited in an appropriate temperature regime, as a thin film.

Closed spaced or sandwich method was developed recently which utilizes the transport of a substance in gaseous form by means of HCl, water vapour or iodide vapour etc along a very short distance of about 100μm. The difference in temperature between the source and the substrate of epitaxial layer is maintained at several tens of degrees. It is possible to use it for the formation of

single-crystal layers of materials which otherwise had not previously been prepared in the mono-crystalline form. This method has a high efficiency (90%). It is employed in the preparation of layers of GaAs, GaP and ternary compounds of the GaAsP type.

Two modifications of the CVD technique were introduced later;
- (i)   a low pressure method, in which the pressure in the reactor tube is lowered by pumping it to the pressure 10 torr range,
- (ii)   a plasma enhanced CVD where, in addition, the gas in the reactor is ionized by an external source (a high frequency electric field) and the reaction proceeds in the plasma that is formed.

The CVD has several advantages as well as disadvantages (Quijada, et al, 1998). The advantages include:
- (i)   Simplicity, achievable, fast recycle times and high deposition rates
- (ii)   Easy control of the stoichiometry of deposited compound films
- (iii)   Easy doping via the introduction of controlled amounts of impurities
- (iv)   Deposition of epitaxial layers of high perfection and high purity.

The disadvantages of CVD include:
- (1) poor understanding of the often very complex thermodynamics and reaction kinetics involved in the deposition process.
- (2) The difficulty in the control of the uniformity of the deposits.
- (3) The often toxic, explosive or corrosive nature of the reactive gases used for the deposition processes.

Spray Pyrolysis

It is a thermally activated reaction between clusters of liquid/ vapour atoms of different chemical species. In this process, the reagents are dissolved in the carrier liquid which is sprayed onto a heated or unheated substrate in form of tiny droplets. In the case of heated substrate, the substrate is maintained at high temperature of about 400˚C. The sprayed droplets undergo pyrolytic

decomposition to form a single crystal or cluster of crystallites of the desired product which the excess solvent and volatile by-products escape in the form of vapour. The hot substrate provides the thermal energy needed for decomposition and the eventual recombination of the species, sintering and crystallization of the crystallites to form a film. Examples include: (i) the formation of cadmium sulphide film by spray pyrolysis of cadmium chloride and thiourea dissolved in water with the substrate at about 300°C (Ezema, et al, 2004); (ii) the formation of tin (III) oxide films by spray pyrolysis of stanic chloride dissolved in propanol and small quantities of HCl with the substrate at 450°C (Raghupathi, et al, 2005).

Some other workers have used the spray pyrolysis technique to deposit thin films which are suitable in both time and temperature. Mondal, et al, 1983 deposited $Sn O_2$ and $Sn O_2$; F thin films on alkaline free coming 7059 substrates, Kale et al, 2004 prepared cadmium selenium selective coatings, Lin et al, 2004 prepared ZnO films and Wu, 2004 deposited cadmium tellurium films, Ezema et al, 2003 deposited beryllium sulphide using chemical bath deposition (CBD) and Rodrique et al, 2005 also deposited antimony sulphide. Generally, low temperature is required for the deposition of amorphous films; and substrate heating may not be necessary in this case.

Plasma Technique
This technique requires a working pressure of between 0.1 to 1.6 torr, and does not require high vacuum condition. The set up for this technique has five basic components, namely: the reactor or deposition chamber, power source, impedance matching network, gas flow regulator and monitoring equipments. The reactor or deposition chamber is where reaction between the gases takes place with subsequent deposition of the films. The impedance matching network makes it possible to transfer generated power more efficiently to discharge. The films are deposited on a negatively biased electrode for this particular version and in another version the films are deposited on both anode and cathode. This

technique has been found very useful in the deposition of many inorganic compounds films such as silicon nitride (Hollahan,et al, 1978).

Some other techniques for thin film deposition include the plasma assisted deposition techniques, which are glow discharge, sputtering, activated reactive evaporation and ion plating. These plasma assisted deposition techniques together with the actual plasma deposition technique itself are fully discussed by Wasa, 1985. It is important to mention that reactive sputtering and plasma techniques are actually hybrid techniques between PVD and CVD. This is because they combine chemical reaction with plasma bombardment which is a physical process.

Sol -gel Thin Film Formation

Sol-gel thin films deposition with sol-gel technique is the oldest commercial application of Sol-gel technology. The use of rear view mirrors produced by sol–gel thin film technologies dated back to 1953 and followed by anti-reflective coatings in 1964 and then architectural coatings in 1969 (Scroeder, 1969, Dislich, 1988). The films produced by this technique are being studied for possible application in electronic and solar energy devices. Sol-gel thin film formed by dipping (or centrifugal) draining is accompanied by vigorous solvent evaporation.

Precursor Sol

Inorganic or metal organic compounds are used as raw ingredients in the sol-gel processes (Brinker, et al, 1992). These compounds are hydrolysed and condensed to form organic polymers composed of M-O-M bonds in aqueous or organic solvents. Inorganic precursors (salts) hydrolysis proceeds by the removal of a proton from an aquo ion

$[MO_NH_{2N}]^{2+}$ to form a hydroxo (M-OH) or oxo (M = 0) ligand (Lange, 1973).

$$[MO_NH_{2N}]^{2+} + pH_2O ==== [MO_NH_{2N-p}]^{2-p} + pH_3O^+ \qquad (4.5)$$
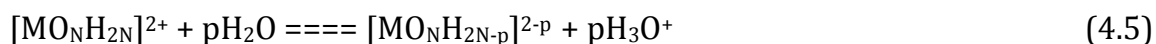
Condensation reaction, involving hydroxo ligands, result in the formation of bridging hydroxyl (M-OH-M) or bridging oxygen (M-O-M) bonds depending on the coordination number of metal M and the acidity of the bridging hydroxyl. At low pH monomeric aquo cations are the only stable species, while at high pH various monomeric anions are the species observed. In the organic precursors, metal alkoxides [M(OR)] are commonly used for sol-gel film formation, where R is an alkyl group C_xH_{2x+1} (Lange, 1973). Here hydrolysis causes an alkoxide ligand to be replaced with a hydroxyl ligand.

$$M(OR)_Z + H_2O ===== M(OR)_{z-1}OH + ROH \qquad (4.6)$$
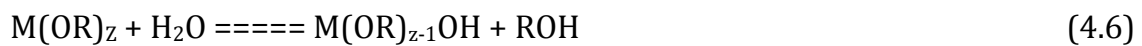
Condensation reactions involving the hydroxyl ligands produce polymers composed of M-O-M or M-OH-M bonds, plus, in most cases, by-products of water or alcohol.

Sol-gel Dip Coating
Withdrawal of a substrate, in the vertical direction, from a fluid sol at a controlled speed V_o characterizes sol–gel dip coating in its simplest manifestations. For the deposition of solid film, there is gravitational draining and solvent evaporation which are accompanied by further condensation reactions. Sol-gel dip coating requires considerable less equipment and is less expensive when compared with conventional thin film forming processes such as CVD, evaporation or sputtering. Several authors (Scriven,et al, 1988, Estrella, et al, 2003 Kushwaha,et al, 2005,) have discussed the sol-gel dip coating.

Spin Coating
The thinning of depositing film by centrifugal draining and evaporation in spin coating makes it different from dip coating. Spin coating consist of four processes which include deposition, spin up, spin off and evaporation (Bindu, et al, 2005). Evaporation in sol-gel normally overlaps the other stages. During the deposition stage an excess of liquid is dispensed on the surface of the substrate. The liquid

flows radially outward, driven by centrifugal force during spin up stage. Excess liquid flows to the perimeter and leaves as droplets during the spin off stage. The rate of removal of excess liquid by spin off slows down as the film thins. Evaporation takes over as the primary mechanism of thinning during the final stage. A film of liquid tends to become uniform in thickness during spin off. It remains uniform provided the viscosity is not shear dependent and does not vary over the substrate. This happens to balance between the two main forces, the centrifugal force, which drives flow radially outward and viscous force which acts radially inward. Spinning creates a strong forced convection in the vapour above the substrate, increasing the evaporation rate. The structure of the film is dominated by the effect of capillarity (Brinker, 1992).

Spin Deposition of Halide and Chalcogenide Films

The solvent-cast technique (spin coating) involves two – step preparation of the film. In order to obtain the amine salt of the chalcogenide, the relevant chalcogenide powders are first dissolved in amines. The solution is dried in a vacuum furnance for 20 hours between $30°C$ and $60°C$. In the second step in order to obtain chalcogen solution used for spin coating, the dried salt powders are dissolved in amide solvent. This procedure has been chosen for the following reasons;

(i)   the highly hygroscopic nature of amine salt, which makes it to pick water from moist air.

(ii)   These amides are insoluble in the amines, thus the cast solution is deposited.

(iii)   Amide solution produces smoother coated surface than amine solution.

This procedure has been adapted to produce chalcogenide films of FeCdS3 (Ezema, 2004), $Pb_{1-x}Sr_xSe$ (Majumdar, 2003), CdZnS (Jae-Hyeong,et al, 2003), $CuGaS_2$ (Solima, 1998), $AgInS_2$ (Ortega-Lopez, et al, 2003), CdZnTe (Ramesh, et al, 2003). A modification of the above procedure was adapted by (Lin Susha, et al, 2004), (Salem, 2002), (Sasaki, et al, 2003) and (Woon-Jo, et al, 2003) which can be used to grow a wide range of chalcogenides and halides films for possible

device applications and also to eliminate the constraints on the As_2S_3 film thickness and quality. In their work, the spinning solution consisted of sodium selenosulphate, arsenic (III) chloride, triethanolamine, ammonia solution, sodium hydroxide, hydrochloric acid, hydrazine hydrate and thioacetamide. For metal modified As_2S_3 films, chlorides of vanadium, cobalt, zinc, indium and antimony were used as dopants. With a solution tetraethyloxthosilicate in methanol, CdS (Kaur, et al, 1980) and $CuInSe_2$ (Jacques, et al, 1996) were prepared by CBD coating on glass slide

Solution Growth Technique.

Solution growth technique has been termed as autocatalytic deposition or electrolysis deposition or chemical bath deposition. It is one of the most cost saving, convenient and simple technique which is easily reproducible. This technique is used to deposit conducting and non-conducting layers from solution by electrochemical processes in the absence of an external field (Quijada, et al, 1998). It exploits the fact that films can be deposited on substrates whether metallic or non-metallic by dipping them into suitable solution baths containing metal salts. The metal ions and non-metallic ions present in solution react with each other to form neutral compounds. The method is based on a controlled precipitation of the desired compound from a reaction solution.

A necessary condition for a compound to be precipitated from a solution bearing its ions is that its ionic product (IP) must exceed its solubility product Ksp.

A sparingly soluble inorganic salt A_xB_y dissociates in a standard solution according to the equation;

$$A_xB_y \text{ (solid)} \rightarrow xA^{y+} + yB^{x-} \text{ (saturated solution)} \tag{4.7}$$
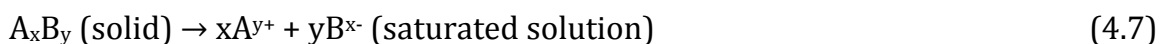
where x and y are integers showing the numbers of cations and anions respectively. The ionic product is given by

$$IP = [A^{y+}]^x [B^{x-}]^y \tag{4.8}$$

where [ ] signifies the molar concentration of the ions at equilibrium and at a given temperature,

$$IP = K_{sp} \tag{4.9}$$

K_{sp} is obtained from standard tables (Lange, 1973).

In order to precipitate the compound A_xB_y, the solution of substance bearing the ions A^{y+} and B^{x-} are brought together in a reaction mixture. Knowing the concentration of one of the ions of such a sparingly soluble compound, in the reaction mixture, and its solubility product K_{sp}, the concentration of the other ion that must be exceeded in order to make $IP > K_{sp}$ can be calculated.

In solution growth technique spontaneous precipitation must be avoided, if thin film is to be grown by controlled ion-by ion reaction. The reaction is slowed down by making use of a suitable complexing agent or ligand in a suitable medium indicated by the pH of the reaction solution. This is the basis of solution growth technique.

When a solution of a suitable complexing agent of a metal is mixed with a solution bearing the metal ions, fairly stable complex ions of the metal are formed. Complex ions are formed when a cation or an anion is joined to one or more ligands by dative bonds. These complex ions of the metal provide ions according to an equilibrium reaction of the form.

$$[M\,(A)_n]^{2+} ==== M^{2+} + nA \tag{4.10}$$

where M is the metal ion with oxidation state 2^+, A is a neutral complexing agent and n is the number of molecules of the complexing agent taking part in complex formation. Thus an appropriate complexing agent can be chosen so that the concentration of the metal ions is controlled by the concentrations of the complexing agent as well as the solution temperature. This ensures that the cations can be released very slowly from their original compounds in a

controlled fashion. At a given temperature, the concentration of the free metal ions is given by Quijada, et al, (1998) as

$$[M^{2+}][A]/[M(A)^{2+}] = K_i \qquad (4.11)$$

where K_i is called the instability constant of the complex.

The experimental set-up of the SGT is simple, cheap and convenient. The glass slide substrate is immersed vertically and at the appropriate centre of the reaction bath. The bath is screened from dust and other environmental impurities by a synthetic foam cover.

The material to be deposited determines the reaction bath composition. One advantage of this technique is that it can be used to deposit uniform films on irregularly shaped substrate and even at points inaccessible through other techniques.

Anderson, (1982) used this technique for the first time to deposit CdS/Cu$_2$S film for infrared applications. Padam et al, (1986), Oladeji, et al, (1997) used the technique to prepare CdS. The work of Oladeji et al (2000), Nair, et al, (1987) was applied for large area deposition and large scale application, this technique gained prominence only in the late 70's and 80's through Bhattacharya et al, (1987). In 1980, several researchers (Bhattacharya, et al, 1982, Oladeji, et al, 1997, Romeo, 1999, Oladeji, et al, 1999) used this techniques for the deposition of several semi-conducting thin film compounds both doped and un-doped such as CdTe, CdSe, CdO, ZnO and mostly CdS for various semi-conducting and photo voltaic applications as well as photo-electrochemical cell. In 1982, silicon hydride (Cody, et al, 1982) was prepared. In 1998, CdS (Choi, et al, 1998) and PdS (Ezema, et al, 2003) were deposited on glass substrate using TEA (Triethanolamine) as complexing agent (Sanjeev, et al, 2005). In 2005, AgSbSe$_3$ (Bindu, et al, 2005) was deposited. In 1998, ZnO:A (Jimenez, et al, 1998) was again deposited. In 1996, CuInSe$_2$ (Zott, et al, 1996) was deposited at the room temperature on glass substrate and in the same year, this technique was

extended to deposition of ternary compound films of $CuInS_2$ (Padam, et al, 1986). In 2004, composite surfaces of $Cd_{1-x}Zn_xS$ (Zhou, et al, 2004) was deposited. The same year $FeCdS_3$ (Ezema, 2004) was again deposited.

Many other reseachers have also employed this method to carry out various depositions in the presence of sunlight. Solar assisted SGT was employed to deposit $CuInSe_2$ (Zweibel, 1990). In 1993 CdTe (Zweibel, 1993), CIS (kapur, et al, 1990) antireflection layer, selective absorbers were deposited and $CuInSe_2$ (Zott, et al, 1996) film was deposited on glass substrate.
 In 1997, Okujagu employed this technique to deposit halide thin films: Sn, Mn, Fe, Pb, Ag, Cu, Zn, and Co, as well as chalcogenide thin films of AgS, NiS, CdS and PbO for spectral selective applications.

In 1995, Uhuegbu, and Okeke deposited iron disulphide thin films using EDTA as complexing agent. Moreover Zhang et al, 1998 characterized $CuInSe_2$ deposited using SGT for industrial applications. In 1997, Eze and Okeke used solar assisted SGT to deposit CoS. A metal halide/chalcogenide film was formed on substrate by an ion – by –ion condensation process.

Thin Films Condensation Formation Mechanism
Three mechanisms of thin film condensation exist, depending on the strength of interaction between the atoms of the growing films and substrate:

(a) Layer by layer mechanism referred to as the van de Merwe mechanism,
(b) three dimensional nucleation, forming, growth and coalescence of islands referred to as Volmer-weber mechanism and
(c) adsorption of monolayer and subsequent nucleation on top of thin layer, referred to as, Stranski-Krastanov mechanism (Glang, 1970).

The ion-by-ion deposition of films on nucleating sites on the immersed surfaces occurs in three phases nucleation phase, known as incubation or induction period, the coalescence phase and the growth phase.

The Volmer-Weber mechanism involves three stages as follows:

(i)   nucleation, during which small nuclei are formed and are statistically distributed (with some exceptions) over the surface.

(ii) Coalescence of the islands (crystallites) and formation of more or less connected network containing empty channels

(iii) growth of the nuclei and formation of larger islands which often have the shape of small crystals (crystallites).

Doping by Chemical Bath Deposition

Doping can be achieved using solution growth technique as in other techniques like vacuum evaporation, sputtering, spray pyrolysis etc, for thin film deposition. The condition for introduction of impurities in the starting chemicals to be incorporated into the film are:

(i)   the impurities must be able to form insoluble halides/chalcogenides under the same deposition conditions

(ii) The ionic product of the halides/chalcogenides must be greater than the solubility product of the complex.

In practice only few dopants satisfy these conditions. The requirements of the above conditions imply that the degree of the purity of the working chemicals is not so important a factor in determining the purity of resulting film when concentration of the impurity is low and the corresponding ionic product is less than the solubility product (Quijada,et al, 1998).

Section 5:

Characterization of Thin Films, Experimental Work and Results

The thickness, composition, solid state and optical characteristics of thin films are tested and measured for the possible applications of thin films and its effectiveness. Methods for determining film properties range from very simple, chemical and mechanical to the very complex electronic and spectroscopic techniques. Spectroscopic method is used to study many film properties such as thickness, film composition, nature of the film, crystallographic orientations, lattice parameters, crystallite size and preferred orientations.

X-ray diffraction methods provide information on the crystalline states, chemical composition, crystallographic orientations and lattice parameters of materials. Qualitative and quantitative evaluation of solid solution, crystal size and preferred orientation of the films are also information which can be provided by x-ray diffraction.

Film Thickness

One of the most important thin film parameters is thickness. Many properties of thin films depend on it: so these properties are used for its measurement. The measurements can be done when the film is being deposited, in that case it is monitored or when the film has been deposited. A number of techniques (Fisher, 1961, Arthur, et al, 1964, Cullity, 1967, Conley, 1966, Runyan, 1976, Gundy, et al, 1976, Osuji, 2003) exist for film thickness measurement. However, the simplest include microbalance (gravimetric method), stylus techniques, interference and optical methods.

Microbalance (Gravimetric) Technique

This method is based on the direct determination of the mass of a film which was deposited onto the substrate. Using a microbalance method a microscopic glass slide substrate was weighed before and after the film was deposited on it. With mass M_1 for the substrate before deposition and M_2 after deposition, the average thickness t was calculated using the measured density of the coated film given by

$$t = (M_2 - M_1)/A\ell \tag{5.1}$$

where A = Lb is the area of the film surface, and t is thickness on one side of the slide and ℓ is the density

$$t = (M_2 - M_1)/2Lb\,\ell \tag{5.2}$$

The density of the bulk material or working solution was approximated to the density of thin film, though the actual density of the thin film was lower because of the porous, and at times, discontinuous nature of most films. Moreover a lot of errors are introduced in the measurement of film area. The mass of the film may be so small, sometime the error introduced in its measurement by ordinary electronic balances can be very significant. Nevertheless, the method gives a good estimate for film thickness greater than 0.1μm, Reather, (1976)

Optical Technique

For a weakly absorbing film on a non-absorbing substrate, the transmittance (T) is given by (Keinath, 1961, Blatt, 1968, Glang, 1970, Theye, 1985)

$$T = (1-R)^2 \exp(-\alpha\,t) \tag{5.3}$$

where R is reflectance , α is the absorption coefficient and t is the film thickness. Taking logarithms in equation 5.3, we have

$$T = \ln[(1-R)^2]/T/\alpha \tag{5.4}$$

t can be calculated when the values of T, R and α are known. For absorbance (A) ≥ 0.10 equation 5.4 can be used to calculate film thickness. For a non-absorbing film on a non-absorbing substrate, the reflectance is given by

$$(n_a - n_s)^2 \cos^2\beta + (n_a n_s/n_f - n_f)^2 \sin^2\beta \qquad R = \qquad (5.5)$$
$$(n_a + n_s)^2 \cos^2\beta + (n_a n_s/n_f + n_f)^2 \sin^2\beta$$

where n_a is the refractive index of the medium of the incident light which is air, n_s is the refractive index of the substrate (glass), n_f is the refractive index of the thin film and

$$\beta = (2\lambda nt)/\lambda_0 \qquad (5.6)$$

t is the film thickness and λo is the wavelength of light. After rearranging, substituting and simplifying, the expression for the film thickness is

$$t = \lambda o/2\prod n \left[\tan^{-1}\left\{ (n_a + n_s)^2 R - (n_a - n_s)^2 / ((n_a n_a/n_f - n_f)^2 - (n_a n_s/n_f + n_f)^2 R)\right\}^{1/2}\right] \qquad (5.7)$$

for A< 0.10 equation 5.7 can be used to calculate the thickness of a non – absorbing thin film. The optical method is treated very well by Keinath, 1961, Marie-Luce Theye, 1985.

Absorbance/ Transmittance Measurements.
Spectrophotometers (Gibson, 1961, Brugel, 1962, Hollas, 1992) are used to measure the absorbance /transmittance of a thin film.
There are different models of this instrument but all of them work on the same principle. The models include SP8-100 UV/VIS PYE-UNICAM, SP3-300 IR PYE-UNICAM, HEλI0Sα UV/VIS PYE-UNICAM, SHIMADZU-UV 3100, PERKIN-ELMER 540B, PERKIN-ELMER λ19, FTIRTM etc.

These instruments work on the principle that when a beam of electromagnetic radiation of initial flux I_o is incident on a transparent specimen, a flux I_x is transmitted. Some part of the incident flux could be absorbed for an absorbing medium while some part could be reflected. The absorbance is read directly from the machine while transmittance and reflectance were calculated from absorbance values while the transmittance is measured directly in the case of IR.

Method of Determining the Composition of Thin Films.

The methods include atomic absorption spectroscopy (AAS), x-ray fluorescence, atomic emission spectroscopy, infrared spectroscopy, spectrochemical analysis, auger spectroscopy (AES), qualitative/quantitative chemical analysis, etc.

Atomic Absorption Spectroscopic (AAS) Method

This method is used to identify the cation present in a thin film sample. It cannot be used to identify the anions. The thin film samples are dissolved in 10ml of 0.1ml HCl or HNO_3. By adding more water, the aqueous solution is then digested and heated until the solvent is evaporated. After necessary adjustments have been made, a pure solvent is used as standard solution to check and adjust the 100% and 0% transmitting settings. The sample solution was taken up in a small curvette which was placed in the atomic absorption spectrometer sample compartment and the lamp turned on for detection of the cation and for analytical absorption measurement to determine the concentration in parts per million (PPM). Different sources of lamp are needed for the detection of different cations and only the cations that have obvious characteristic absorption at certain wavelengths represented by the lamp can be detected. A good example of AAS equipment is PERKIN-ELMER spectrometer 2380.

X-Ray Fluorescence

There are two experimental methods of x-ray spectroscopic analysis namely wavelength dispersive and energy dispersive x-ray spectrometry (Gilfrich, 1974). The source for both is x-ray photon which is used to excite a sample which emits its characteristics x-ray.

The separation of the characteristic x-ray lines according to their energies could be achieved with the use of high resolution Si (Li) detectors. The separation leads to energy dispersive x-ray fluorescence (EDXRF). It is useful in qualitative and quantitative elemental analysis of solid or liquids. The basis of the operation of an EDXRF spectrometer includes the collection and display of information for several elements (from sodium to uranium) in a sample. The versatility of the

technique is it's rapid real time multi-elemental detection capability for various samples. This is accomplished by adjusting the energy of the excitation radiation just above the absorption edge of the element of interest, leading to high sensitivity and selectivity in the analysis. The energy dispersive has simplicity of instrumentation, economy of analytic line intensity and feasibility of simultaneously accumulation and display of the entire x-ray spectrum. There is a solid detector on the x-ray analytical scene that creates interest on the energy dispersion (Bertin, 1975). Low power x-ray tube can be used as a source for energy dispersion.   Moreover secondary monochromatic radiation radio-isotopes and ion beams are alternative sources for the energy dispersive mode (Bertin, 1975). The method, (EDXRF), is one of the recent techniques developed as a result of the general availability of sealed radio-isotope source.

Generally energy dispersive spectrometer consist of an excitation source, high voltage power source, pre-amplifier, amplifier, single or multi-channel analyzer. The characteristic peaks are resolved from the spectrum by pulse height analysis. The present work was performed at the Centre for Energy Research and Training, Ahmadu Bello University, Zaria where the following radio-isotope 25mCi Fe-55, 25mCi Cd-109, 30mCi Am-241 were available.

25mCi Fe-55, 25m CiCd-109 were used for excitation of the characteristic K-lines of light and medium elements. Light elements up to chromium Z =24 can be detected by the use of Fe-55. Medium elements from Germanium Z=32 to Molybidium Z=42 are effectively executed by Cd 109 sources.

Infrared Spectroscopy
Infrared (IR) spectroscope is the most frequently used instrumental technique in organic laboratory courses and is extensively used in inorganic chemistry as well. The common type is the double beam dispersive instrument. However the fourier transform infrared (FTIR) is rapidly gaining popularity (Szafra,et al, 1991). The FTIR spectrometer has two advantageous factors; a FTIR uses an

interferometer instead of a monochromator, and the output data from a FTIR is stored in digital form in a computer memory and can be manipulated. Quantitative analysis by infrared absorption spectroscopy involves the use of the absorption law common to all absorption spectroscopic technique (Brugel, 1962),

$$\log (I_o/I_t) = \alpha \, cl \qquad\qquad\qquad (5.8)$$

Where logarithm of the ratio of the incident (I_o) to the transmitted (I_t) radiation is dependent on absorption co-efficient (α), of the sample, the sample concentration (c) and the cell length (l).

Using a spectrometer, it is possible to examine absorptions beyond 16μm. This is because the vibrational energy decreases with increasing mass, hence, this region could be useful for the examination of low energy vibrations occurring in both organic (especially organo-metallic) and inorganic substances. From the examination of a large number of inorganic compounds, it was apparent that particular anions were absorbed in certain, rather, narrow regions of the infrared spectrum. From these observations, it was clear that such correlations were useful in establishing qualitative identification (Conley, 1966). The films are mulled in a liquid material that does not interfere in the IR region of interest. The material usually used is Nujol (Szafran,1991). Nujol has absorbance in the IR region corresponding to C-H bonds. In the alternative and often better, 5mg of the sample is mixed with 150mg of potassium Bromide (KBr) and placed in a pelled press cell. At high pressure, the KBr will flow and seal the sample in a window of salt. Since KBr is transparent to IR radiation, the IR spectrometer will detect only the sample. The cell should be cleansed immediately because KBr is corrosive and could damage the cell. In this work Nujol was used as mull material on FTIR spectrometer. For interpretation of spectrum (Conley, 1966, Szafran, et al, 1991) alongside with Aldrich library of FTIR spectral (Aldrich chemical company) and the saddler IR spectra compendia (saddler) published spectral could be consulted.

For qualitative analysis, the mull technique is rapid and convenient but quantitative data are difficult to obtain, even when internal standard is incorporated into the mull.

Qualitative/Quantitative Chemical Analysis (QCA)

QCA (Fisher, 1961, Arthur, et al, 1964) is the most direct and least expensive method for determining the composition of thin films. To determine the chemical formula of a sample by quantitative chemical analysis the following procedure is followed

  i)   The sample is dissolved in about 5ml of 0.1M HCl
  ii)   The sample is analyzed to get the percentage composition of each element.
  iii)   The percentage of each substance is divided by its atomic weight.
  iv)   The bigger result is divided by the smaller result (or in cases where more than two elements are present, each result is divided by the least result).

From the resulting ratio the chemical formula of the sample is obtained. Sometimes it will be required to find out just the cations and/or the anions present without determining the chemical formula. In such a case it sufficient to use the simple qualitative tests to identify the cations and the anions present in the sample.

Crystallographic Structure and Topography

The crystallographic studies, x-ray diffraction (XRD) and transmission electron microscopy (TEM) techniques are the most widely used.

The x-ray diffraction technique (Cullity, 1967, Runyan, 1976) is essentially non-destructive and does not require elaborate sample preparation. Conventional XRD instrument is used to analyze specimen with thickness $\geq 10^{-7}$m which utilizes electron diffraction (Gundy,et al, 1976) while thin film diffractometer is

used to analyze specimen with thickness < 10^{-7}m. Modern equipment permits thickness down to 10^{-8}m to be analyzed

XRD can be used to ascertain if a thin film is amorphous or composed of randomly oriented poly-crystals or single crystals. Amorphous film gives no well-defined diffraction rings, while randomly oriented poly-crystals give well defined diffraction rings. From the width of the diffraction lines it is possible to infer the average grain size D of the crystallites in the polycrystalline films according to the equation (Warren, 1963, Klug, et al, 1974).

$$D= K\lambda/\beta\cos\theta \qquad\qquad\qquad\qquad\qquad (5.9)$$

where λ is x-ray wavelength in Å, β is the real diffraction broadening, K is a constant and is equal to 0.9, when β is measured at half-maximum of the diffraction peak and θ is the Bragg's angle. The dimension of crystallites in the range of 5-120nm may be determined in this way. Single crystal films or identically oriented poly-crystals give rise to round diffraction spots called lave patterns. The spot are distorted as the orientation of the poly-crystal deviates from perfection. They take an elliptical shape and new spots appear. The elliptical spots join to form the diffraction rings in an extreme case of complete randomization. There arise missing or low intensity rings if one axis of the crystal remains the same while the orientations of the other axes are random.

For XRD analyses, a scanning θ-2θ, diffractometer Philips PW 1730 is often used. It has a long fine focused sealed- off x-ray tube with a copper angle of 12° to reduce target self-absorption for high incident intensity. The values for the various reflections are read from the resulting trace and the d-spacing of the reflecting planes calculated Data analysis can be done manually, and with the aid of the joint committee on powder diffraction standard (JCPDS) powder diffraction file (PDF).

Transmission Electron Microscopy (TEM)

The TEM has been in use since 1956 and has been used to identify and study dislocations in thin films. Various properties which can be studied by this technique and its variations (Hall, 1966, Wyckoff,1949, Heidenreich, 1964) include lattice defects such as stacking faults dislocations, vacancy, clusters etc. The varieties of this technique include scanning electron microscope (SEM), scanning transmission electron microscope (STEM) and analytical transmission electron microscope (ATEM).

In scanning electron microscope (SEM) a finely focused beam of electrons are scanned in a rectangular raster over a specimen. When the electron interacts with the atoms of the specimen they are reflected (back scattered electrons) or they can cause the ejection of much slower elections (secondary electrons). Either of the group can be used to form a picture. The usual method is to use an electron detector to form an electric current proportional to the number of such electrons and use this current to modulate the intensity of an oscilloscope or television which is scanned synchronously with the beam raster. The pictures produced by such microscope are of the surface topography of the specimen.

The secondary electron mode of the SEM is usually more acceptable in the surface topographical determinations of a thin film. In this case electron emission can occur only to a depth of 10^{-9}m, thereby giving a picture that is a true representation of the specimen surface features. The pictures produced give the illusion of three dimensions. A magnification achievable by this technique is $3x10^{-9}$m.

Surface Structure

The surface structure of thin films can be studied using some techniques which include low energy electron diffraction (LEED), reflection high energy electron diffraction (RHEED), field emission microscope (FEM), ultraviolet photoelectron spectroscopy (PES) (Duke,1981, Vook, 1981). Some of the properties that can be

studied include the determination of work function, corrosion catalysis and the absorption of gaseous elements on otherwise clean surface.

LEED TECHNIQUE

This is used for epitaxial (single crystal) film. LEED is the coherent reflection of electrons in the energy range 5eV-500eV from the uppermost few atoms of layers of crystalline solid. In this technique (Lander, 1965, MacRac, 1966) low energy electron is made to impinge on the surface of film, they are scattered and accelerated to a fluorescent screen which displays the diffraction pattern. This technique only gives rise to a two-dimensional surface structure since slow electrons do not penetrate much beyond the first atomic layer. By analyzing the diffraction pattern, the dimensions of the surface structure and the arrangement of atoms could be obtained.

RHEED TECHNIQUE

This is used for all types of films including the amorphous and polycrystalline. This is good for thicker films. It utilizes a glancing angle electron beam on the film surface which scatters it onto a fluorescent screen and diffraction is exhibited. The energy of the electro beam is 10-100keV. The beam can penetrate to deeper layers of the film, thereby making the study of such layers possible.

Photo Electron Spectroscopy (PES)

This PES, is a powerful tool for determining the electronic structure of surfaces. An example, is the intrinsic surface of states on semiconductors and metals, and the adsorbed atoms and molecules on various surfaces. The sensitivity to observe surface states and mono-layers or sub-mono-layers quantities of absorbates, results from the very short $(5-15)x10^{-10}$m escape depths of the projected electrons that are measured.

Optical Microscopy.

The principal method for investigating the morphology of the surface of a thin film in an optical and mechanical microscopy. Morphological analysis can be determined using optical microscopy (Weston, 1962, Richardson, 1971). In microscopy the characterization of a surface means topography, elemental composition and solid state structure determination.

There are accessories for the light microscope that greatly enhance its ability to resolve in detail, differentiate different composition or increase contrast (McCrone, 1974). From the technique known as photomicrography (Weston, 1962), photomicrograph of the film surface and corresponding topographical structures may be obtained

The photomicrographs can be used to calculate the grain size as follows (Voort, 1984). First a circle of diameter 79.8mm (with an average area of 500mm^2 corresponding to the actual area of 0.5mm^2 of a film surface) is drawn on a photomicrograph taken at 100x magnification or on a transparency placed on it. At least 50 grains must be contained in the circle. A smaller magnification must be used if the number of grains in the test area is less than 50. The number of grains n per mm^2 of the micrograph is determined from the relation (Geller, 1977).

$$N = 2^{N+3} \tag{5.10}$$

where N is the grain number. When n >10, a different magnification must be used. If m_1 is the number of grains intersected by the circular line and m_2 is the number of grains M at 100 x magnification for equiaxed grains is given by

$$M = m_2 + 0.5m_1 \tag{5.11}$$

The total number of grains per mm^2 of the surface of a photomicrograph for 100 x magnification is given by

M = 2m   (5.12)

With a magnification other than 100x gives

M= $2(g/100)^2$ mg   (5.13)

Where g is the actual magnification employed and mg is the number of grains calculated with this magnification. For non-equaxed grains the average number of grains M_{av} is determined from the three most characteristic fields of view namely longitudinal M_L, transverse M_t and normal M_n so that

M_{av} = 1/3 $[M_L+M_t+M_n]$ (5.14)

The average grains area S_{av} and average grain diameter D_{av} are respectively given by

S_{av} = $1/M_{av}$ (5.15)

D_{av} = $1/(M_{av})^{1/2}$ (5.16)

In this way the average size of a thin film can be estimated.

X-ray and ultraviolet microscope (Gottfried, 1961, Newkirk et al, 1966) afford better resolution than the optical microscopes. This is because the increase in the resolution of fine structures in a specimen is inversely proportional to the wavelength of radiation illuminating the specimen. X-ray and UV radiation have shorter wavelengths than visible light. UV microscopes also have the added advantage that many substances that are practically transparent to visible light absorb heavily in the UV, thus making the micrographs of the specimen more visible.

Experimental work and Results

In the preparation of metal halide and chalcogenide thin films by solution growth technique, care was taken to produce hydroxide free films (Uhuegbu, et al, 1995, Eze,et al, 1997). The elimination of the incorporation of solid phase metal hydroxide into the thin film was obtained by optimizing both the chemical bath and deposition time. The chemical bath constituted a source of cation, a source of

anion, a complexing agents for the deposition of metal halide/chalcogenide films and distilled water. All the reagents used were of analytical reagent (A.R) grade. The pH of the initial bath solution was taken.

Glass rod stirrers were used to stir the reaction bath thoroughly before the introduction of the glass slides as substrate. The magnetic stirring also can be used to stir the mixture. Synthetic rubber foam was used as cover to the reaction bath to protect it from dust particles and other environmental impurities as well as to suspend the substrate into open bath. This arrangement did not allow for an airtight reaction bath. This prevented condensation on the inner surface of the cover. The experiment was carried out at room temperatures ($\sim300K$).

To produce the test sample, the solutions were poured into a 50 ml glass beaker and the depositions were made on 26 mm x76 mm x1 mm commercial quality glass microscopic slides. Prior to the deposition, the slides were thoroughly cleaned before dipping into the reaction bath. To do this, the substrates were degreased by dipping them in concentrated HCl and HNO_3 in the ratio 3:1 respectively. They were brought out after 48 hours and dipped in cold detergent solution where they were subjected to scrubbing with soft rubber sponge. Thereafter they were rinsed in distilled water and drip dried in air, they were then weighed using the AE 166 analytical balance. The degreased, cleaned surface has the advantage of providing nucleation centres for the growth of the films, hence, yielding highly adhesive and uniformly deposited films.

The substrates were dipped vertically into the centre of the reaction baths in such a way that they did not touch the bottom or walls of the bath containers. Several variations of the bath constitutions of each compound whose films were to be deposited were employed. For a chosen standard reaction bath for such a compound the substrates were allowed to stay in the bath for different dip times. This allowed the growth condition to be optimized and the baths standardized. After deposition, the films were washed in distilled water, drip dried in air and weighed. In this work, we deposited the following ternary thin films: FeCuS, FeZnS, PbAgS, CuAgS, and CuZnS.
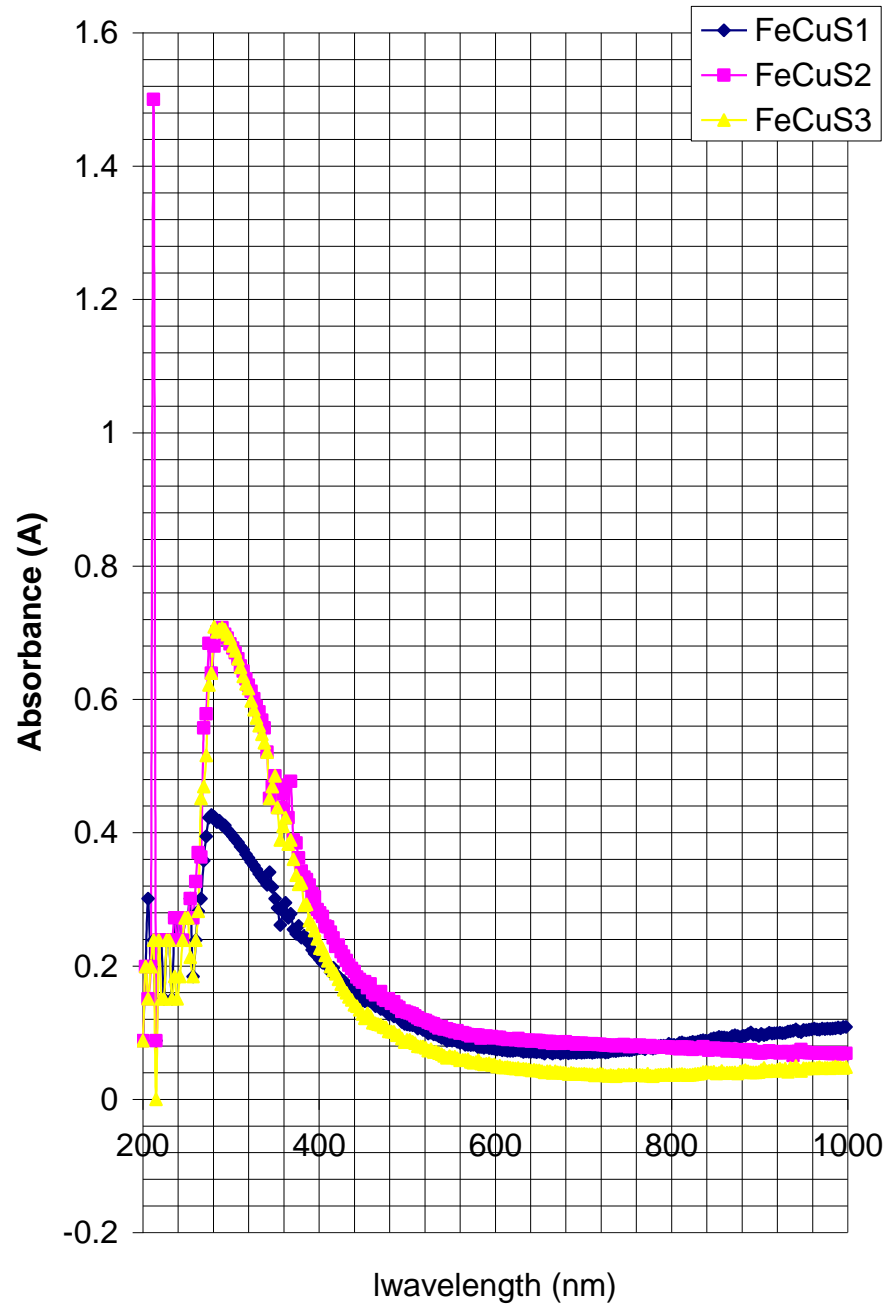
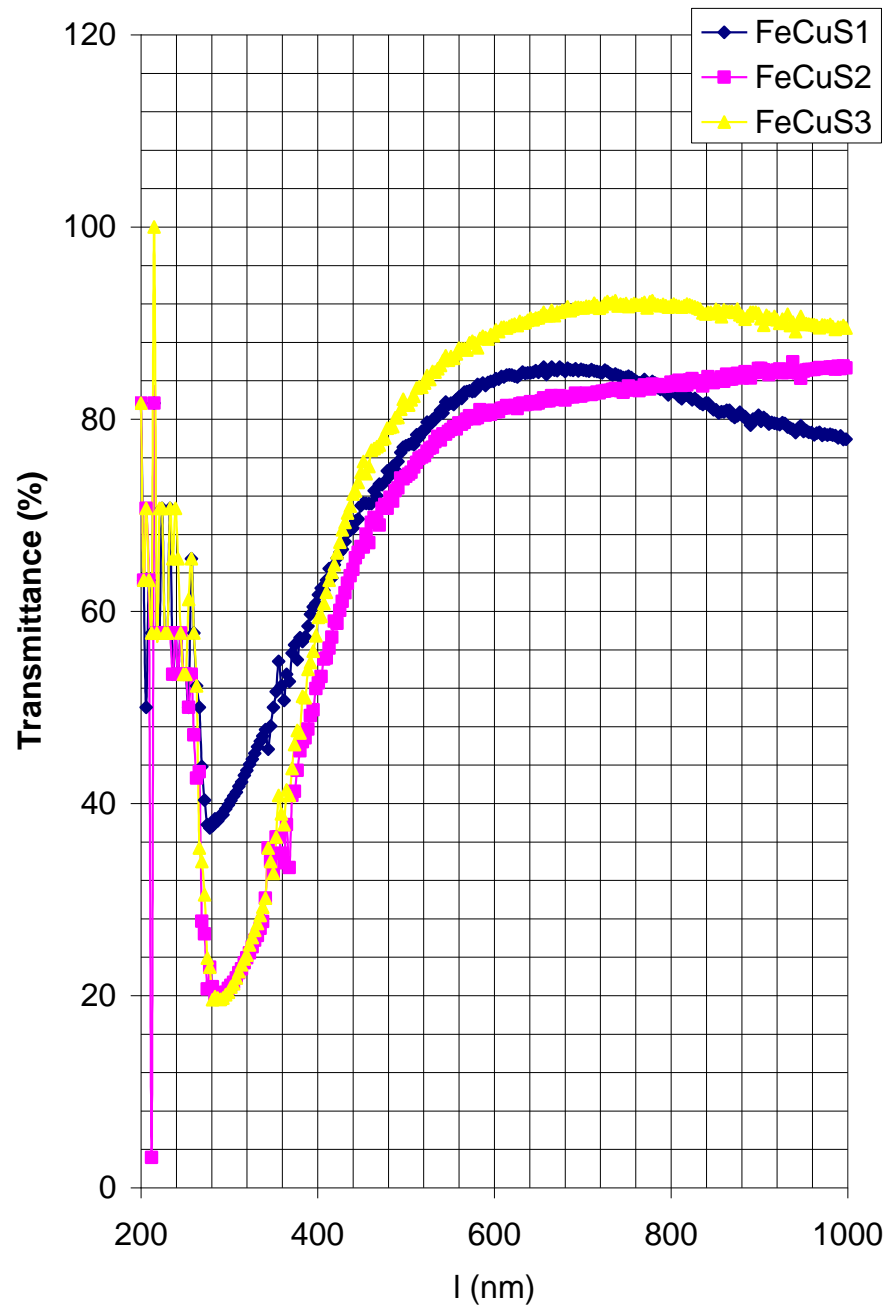Figure 5.1 : Absorbance (A) as function of wavelength for FeCuS Thin Film

Figure 5.2   : Transmittance (T) as function of wavelength for
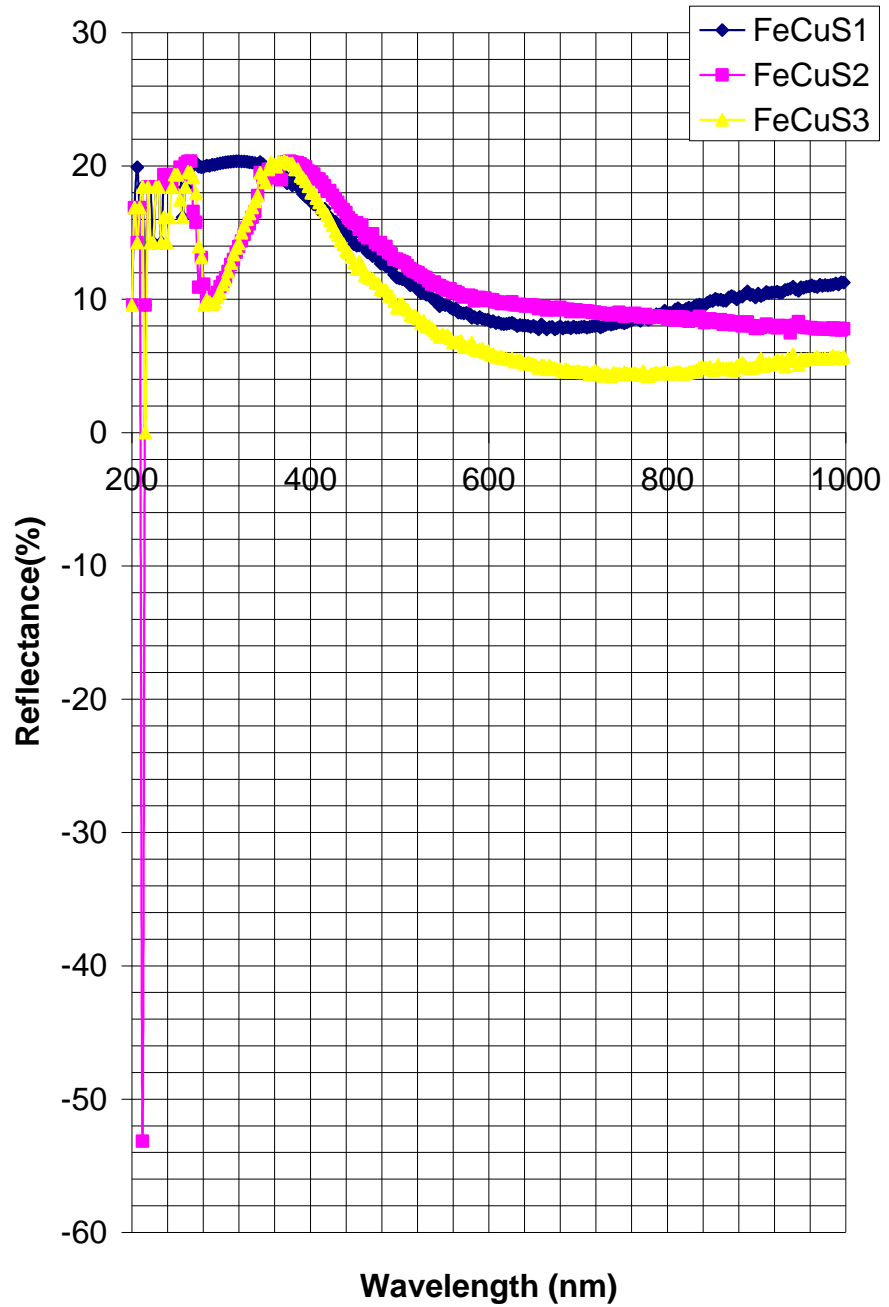FeCuS Thin Film

Figure 5.3   :Reflectance(R) as function of wavelength for
FeCuS Thin Film
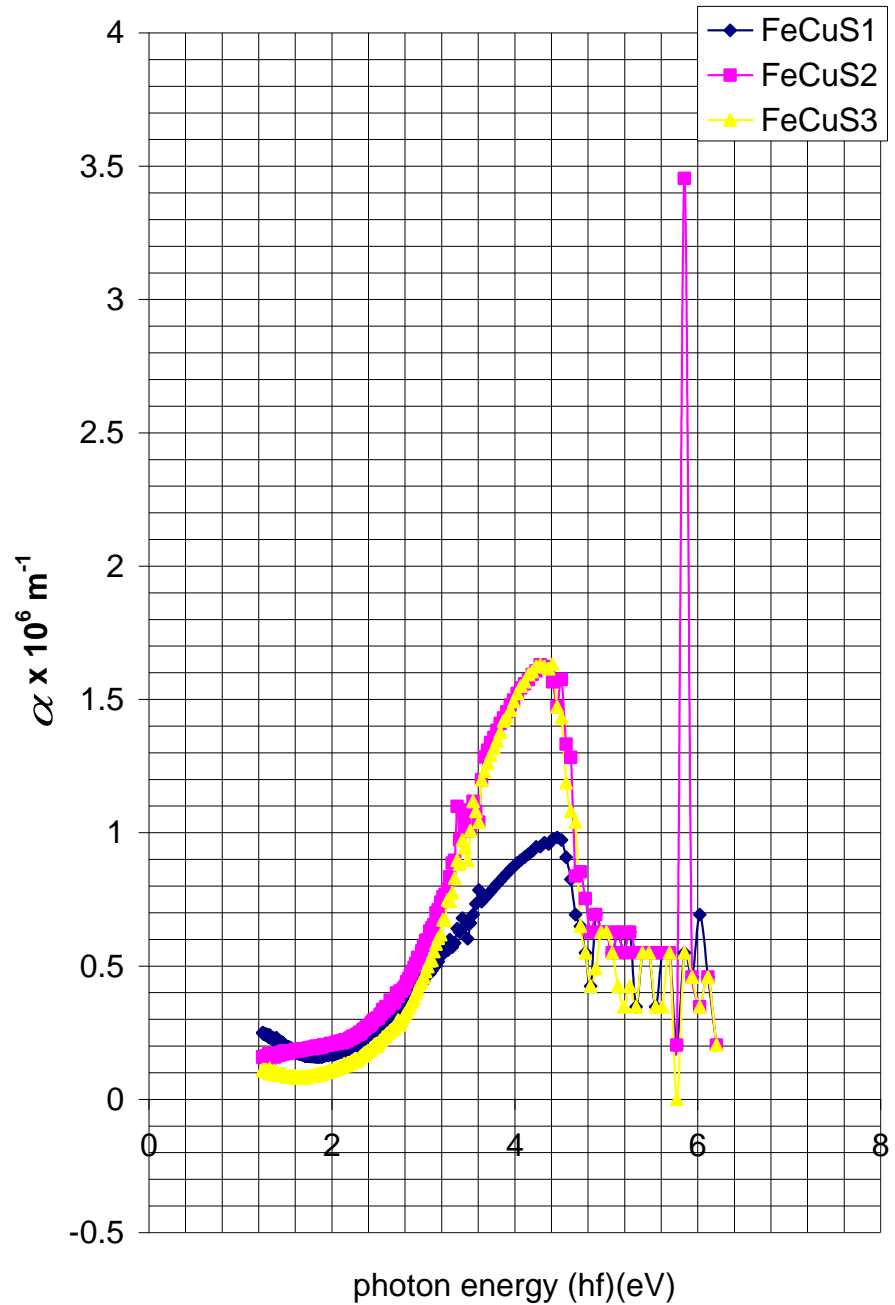
Figure 5.4 : A Plot of absorption Coefficientas a function of
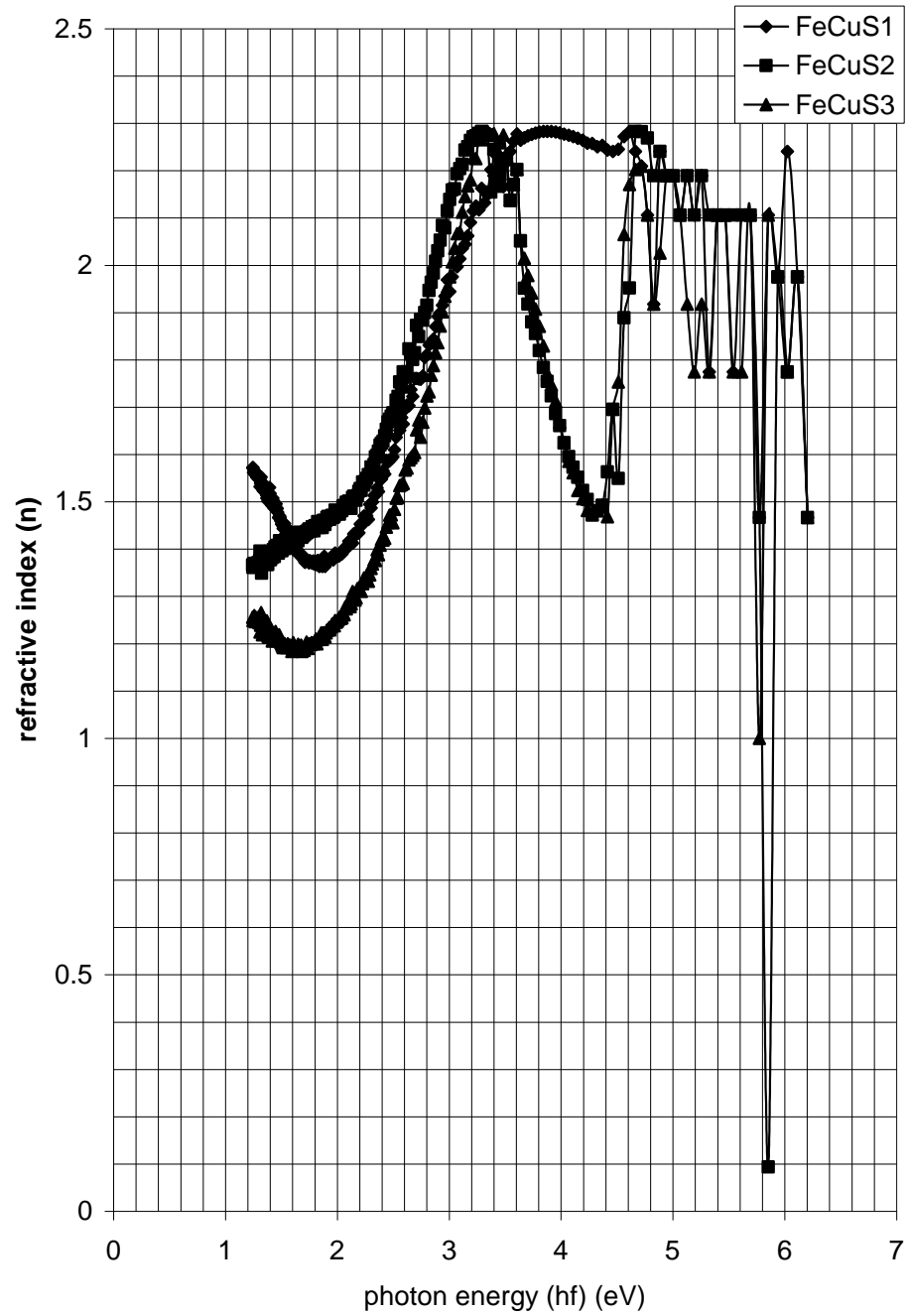Photon Energy (hf) for FeCuS Thin Film

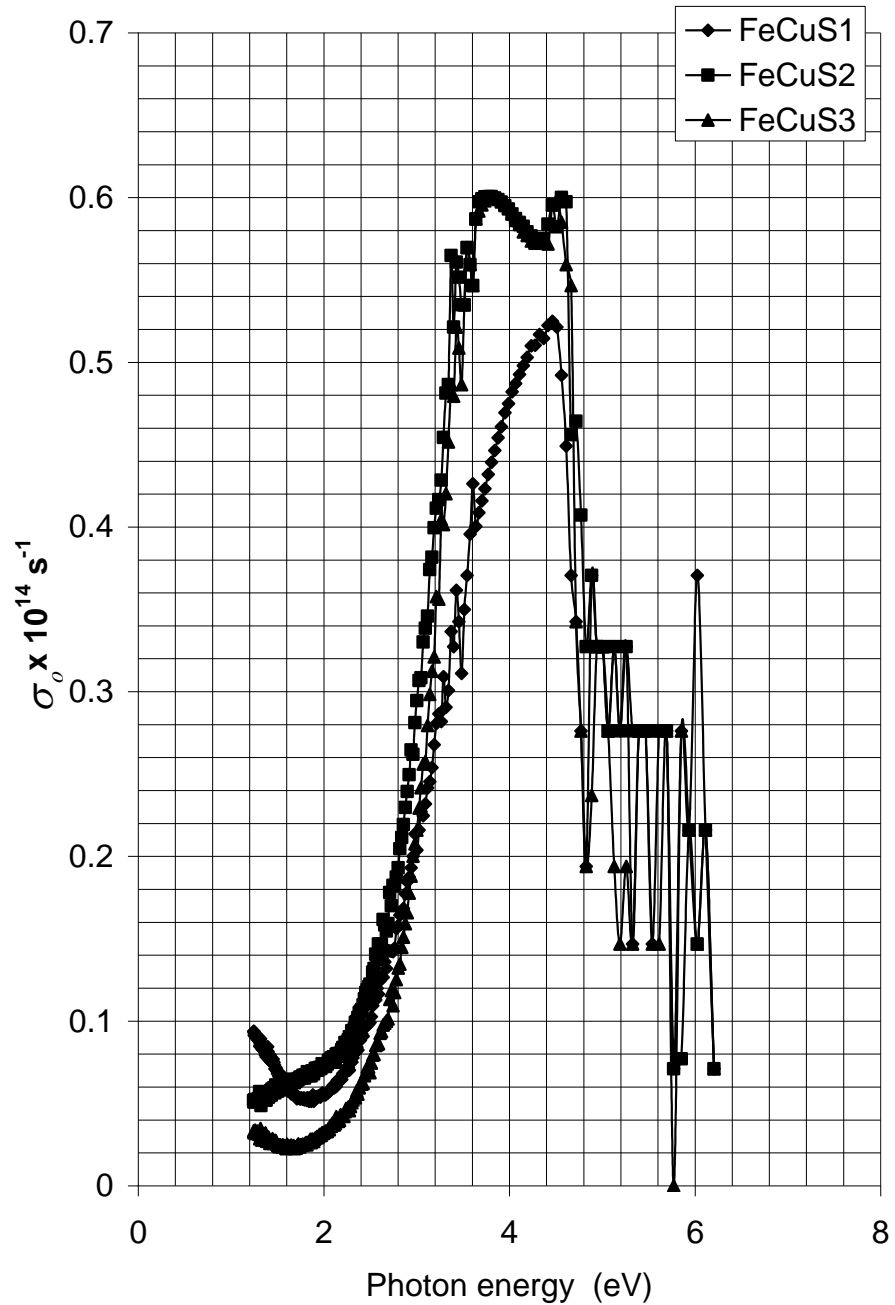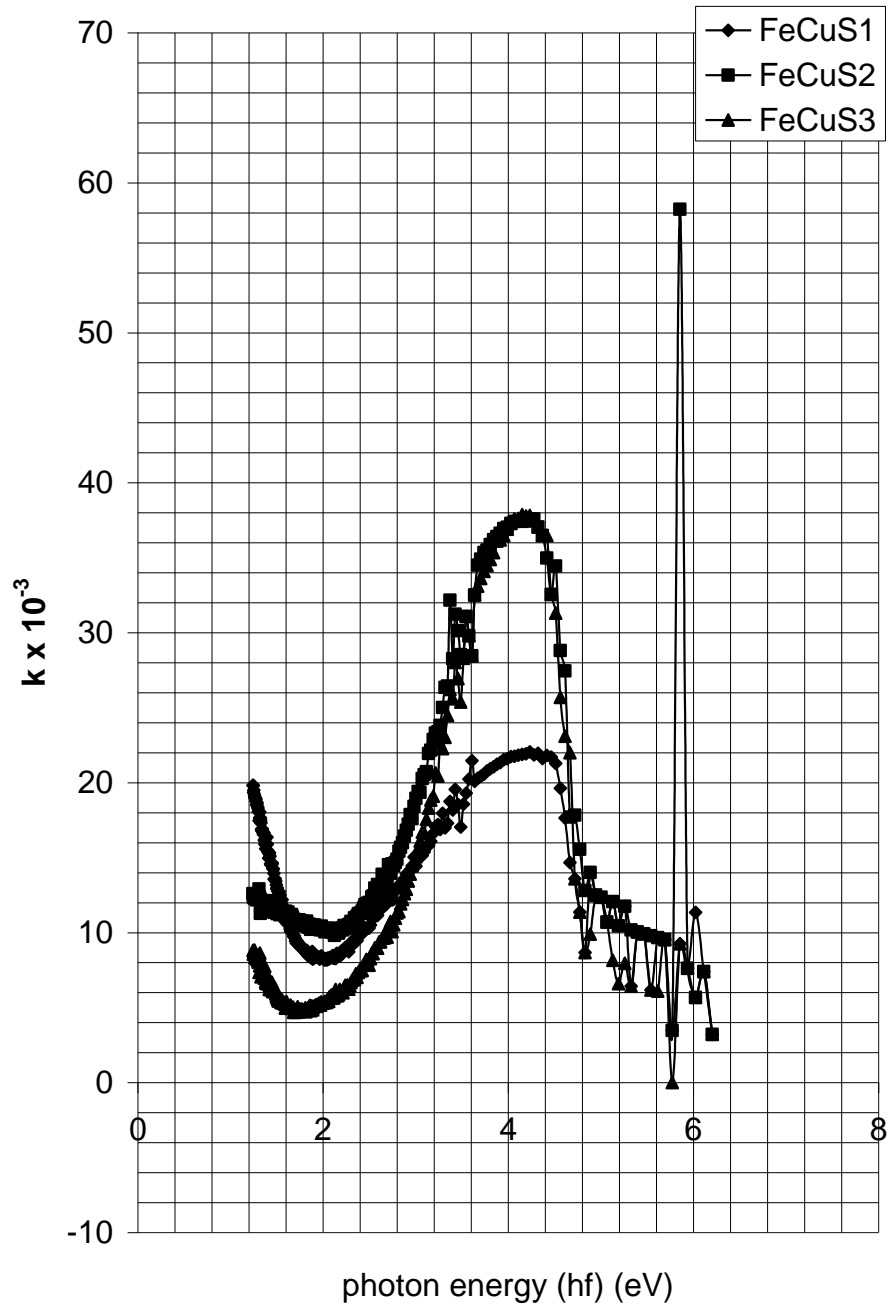Figure 5.5 : A Plot of Refractive index (n) as a function of Photon Energy (hf) for FeCuS Thin Film

Figure 5.6 : A Plot of Optical conductivity as a function of
Photon Energy (hnf for FeCuSThin Film

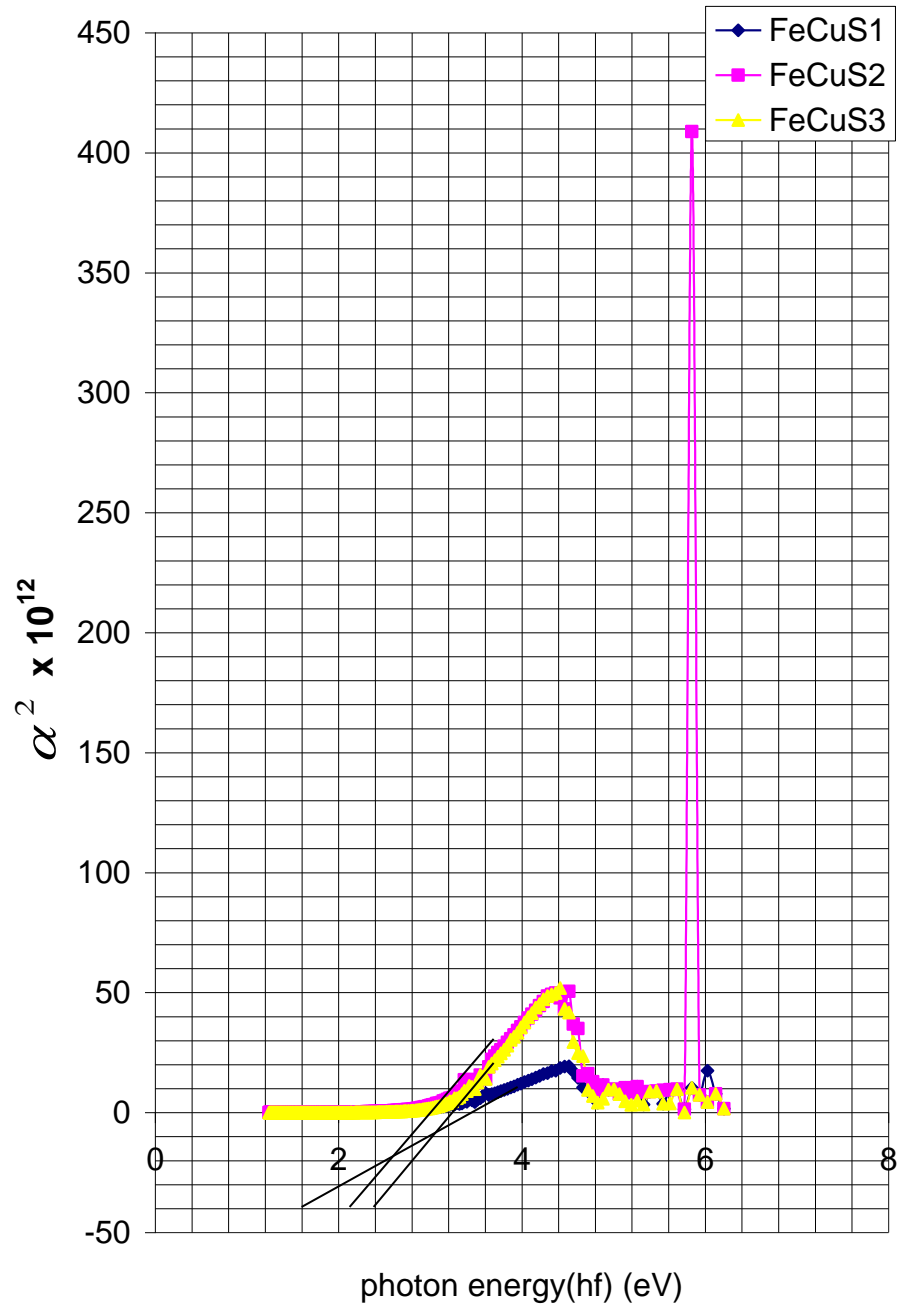Figure 5.7 : A Plot of Extinction coefficient as a function of Photon Energy (hf) for FeCuS Thin Film

Figure 5.8: A Plot of [absorption Coefficient)^2 as a function of Photon Energy (hf) for FeCuS Thin Film
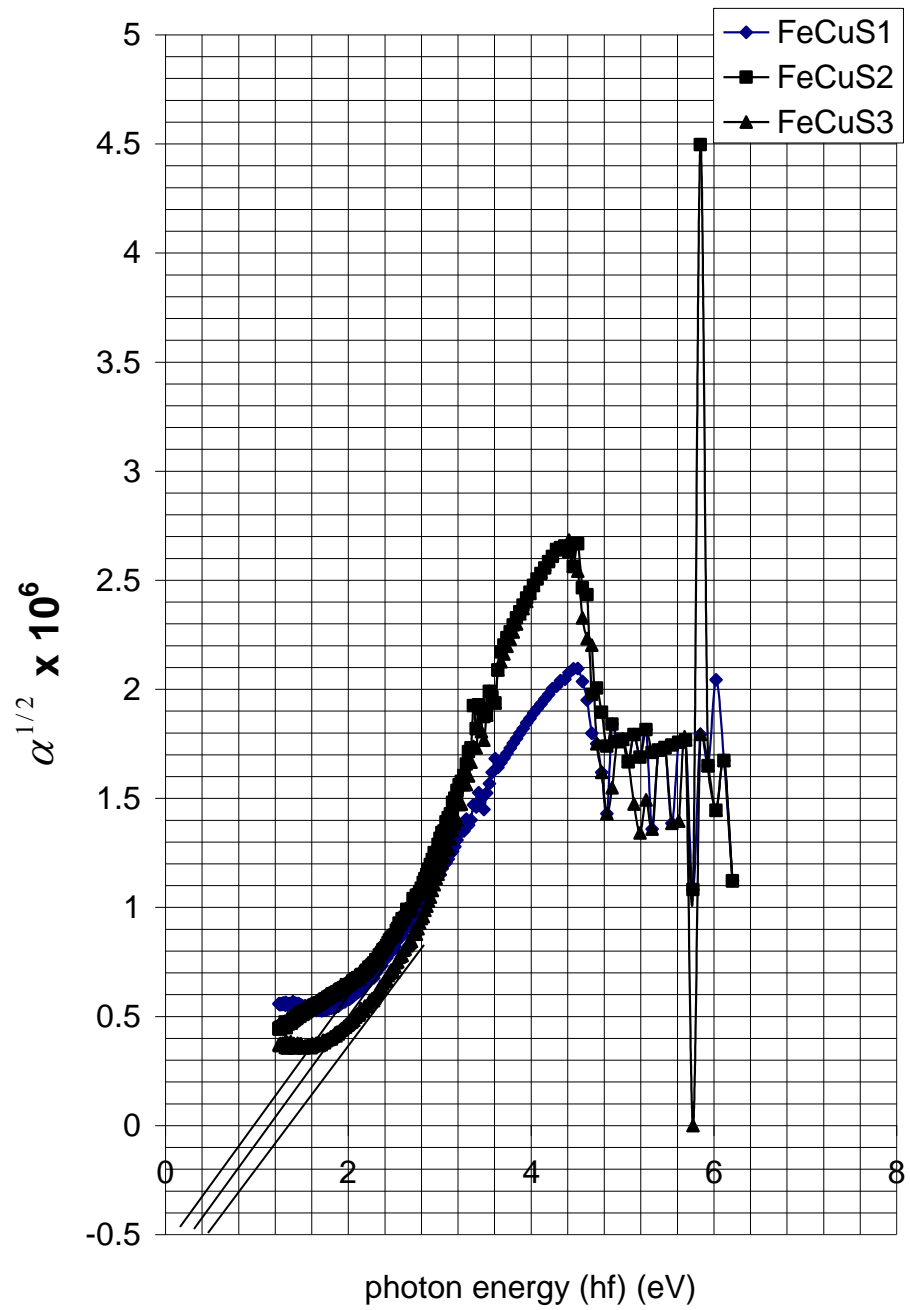
Figure 5.9 : A Plot of (absorption Coefficient)$^{1/2}$ as a function of Photon Energy (hf) for FeCuS Thin Film
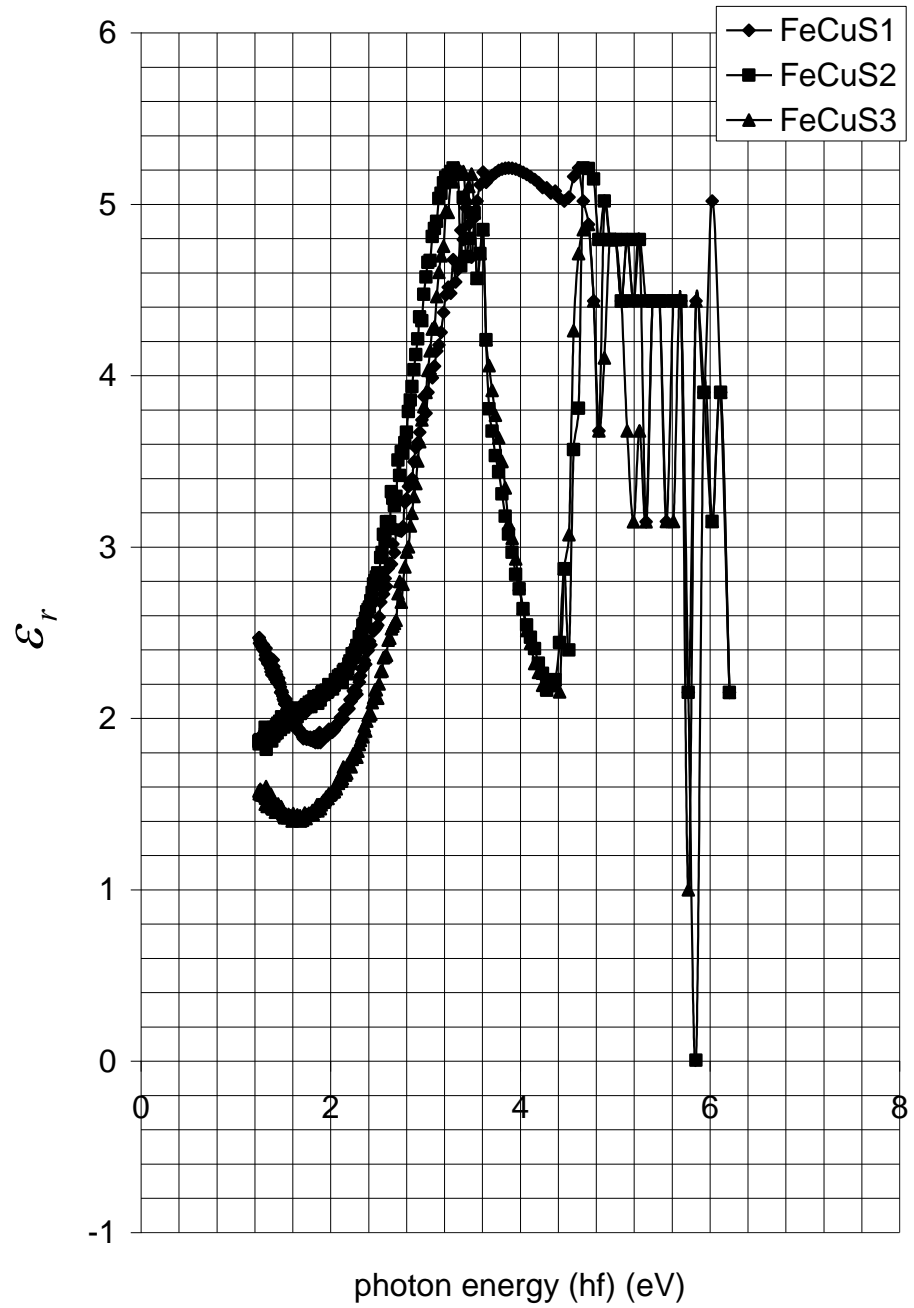
Figure 5.10 : A Plot of Dielectric constant(real part) as a function of Photon Energy (hf) for FeCuS Thin Film
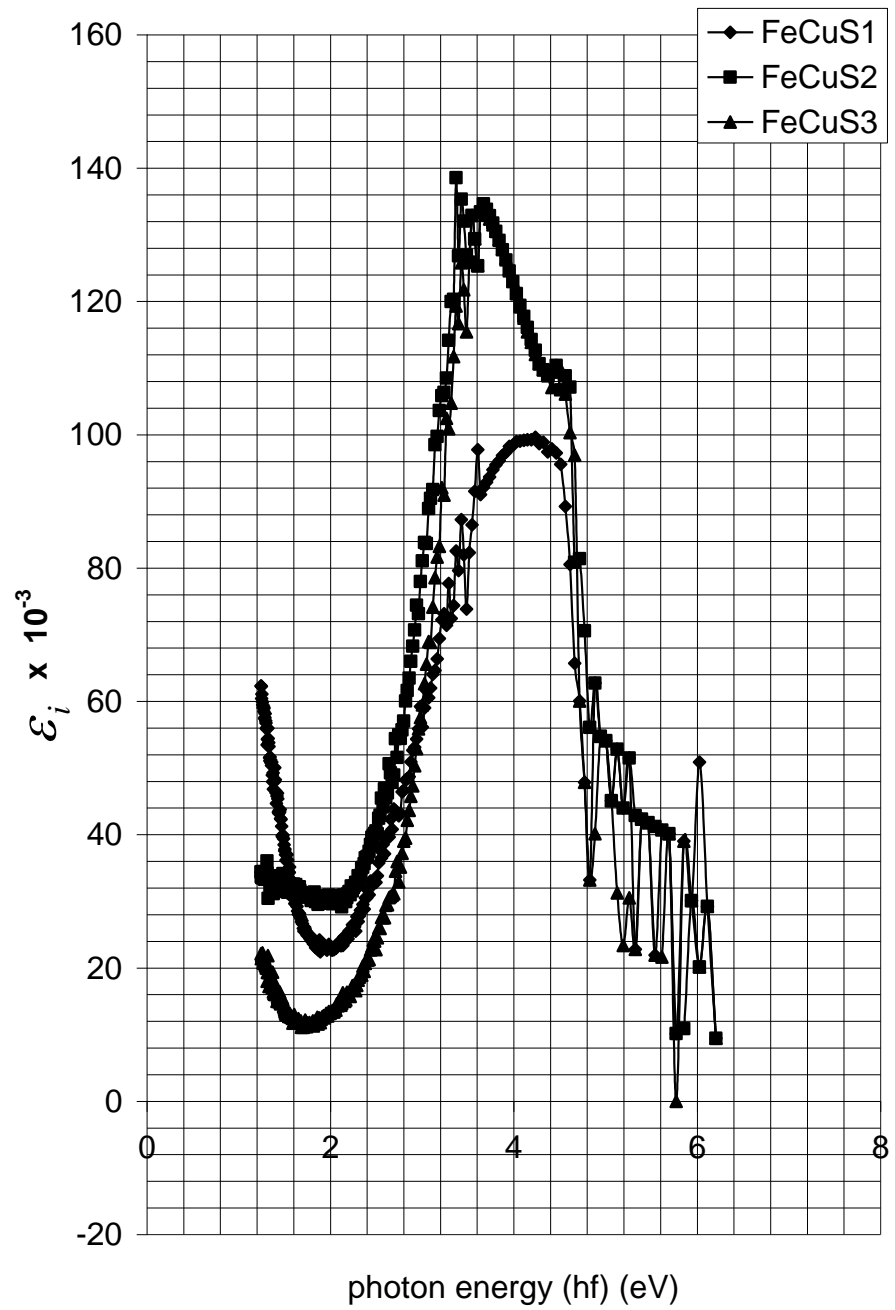
Figure 5.11 : A Plot of Dielectric constant (imaginary part) as a function of Photon Energy (hf) for FeCuS Thin Film

Results

Eleven graphs each were plotted, analyzed and the results presented for the five films. However, only the graphs of FeCuS as shown in figures 5.1 to 5.11 are included in this presentation.

The Spectral Analysis Results

Only the plots of absorbance, transmittance and reflectance versus wavelengths for FeCuS are shown in figures 5.1 to 5.3, while the results of FeCuS, FeZnS, PbAgS, CuAgS and CuZnS, are presented (Uhuegbu, 2010a) absorbance was high in UV and low in VIS-NIR region, while the transmittances were low in UV-region and high in VIS-NIR regions. The reflectances were high in UV-region and low in the VIS-NIR regions. As a result of these properties, UV radiation is screened off and the infrared and visible radiation is admitted into the building by the films. The films are also suitable for eye glass coating for protection. These findings are in agreement with that of Ezema (2004) for the FeCdS films Ezema et al (2006) for the MgCdS films.

Other Optical Properties

The graphs of absorption coefficient, refractive index, optical conductivity and extinction coefficient for FeCuS only were presented in figures 5.4 to 5.7 and the results of FeCuS, FeZnS, PbAgS, CuAgS and CuZnS were discussed. The absorption coefficient ranged from 0.1×10^6 to $1.65 \times 10^6 m^{-1}$, $0.2 \times 10^6 m^{-1}$ to $2.3 \times 10^6 m^{-1}$, $0.5 \times 10^6 m^{-1}$ to $0.9 \times 10^6 m^{-1}$, $0.5 \times 10^6 m^{-1}$ to $1.28 \times 10^6 m^{-1}$ and $0.24 \times 10^6 m^{-1}$ to $1.6 \times 10^6 m^{-1}$, respectively. The real part of the refractive index ranged from 1.2 to 2.3, 0.72 to 2.3, 0.1 to 2.3, 1.94 to 2.28 and 1.6 to 2.3, respectively. The corresponding values of optical conductivity ranged from $0.03 \times 10^{14} s^{-1}$ to $0.6 \times 10^{14} s^{-1}$, $0.07 \times 10^{14} s^{-1}$ to $0.6 \times 10^{14} s^{-1}$, $0.06 \times 10^{14} s^{-1}$ to $0.6 \times 10^{14} s^{-1}$, $0.24 \times 10^{14} s^{-1}$ to $0.6 \times 10^{14} s^{-1}$ and $0.12 \times 10^{14} s^{-1}$ to $0.6 \times 10^{14} s^{-1}$, respectively. The extinction coefficient ranged from 0.005 to 0.038, 0.004 to 0.056, 0.010 to 0.140, 0.025 to 0.064 and 0.008 to 0.082, respectively (Uhuegbu, 2008, 2009, 2010b, 2010c, 2010d,2010e,). These properties make the films suitable for: photovoltaic

application, solar thermal conversion, protective coating materials. This is in agreement with the findings of Ezema (2004), Jacques et al(1996), Pawar et al(1986), Kushwaha et al (2005), Bindu et al (2005) etc. for similar films.

Solid State Properties

The graphs for the properties below for the five films were plotted and only that of FeCuS shown in figures 5.8 to 5.11 were included here. The results revealed the following; the direct band gap ranged from 2.4eV to 2.8eV for FeCuS, 2.9eV for FeZnS, 1.5eV to 2.1eV for PbAgS, 2.3eV for CuAgS and 2.2eV to 2.4eV for CuZnS. The values of the indirect band gap were in the range 0.6eV to 1.0eV for FeCuS, 1.9eV for FeZnS, 0.3eV to 0.8eV for PbAgS, 1.1eV for CuAgS and 0.4eV to 0.9eV for CuZnS. The real part of the dielectric constant ranged from 1.4 to 5.2, 0.7 to 5.2, 0.4 to 5.2, 3.8 to 5.2 and 2.2 to 5.2, respectively, while the corresponding imaginary part of the dielectric constant ranged from 0.008 to 0.136, 0.008 to 0.164, 0.010 to 0.390, 0.100 to 0.290 and 0.030 to 0.360, respectively (Uhuegbu, 2011a, 2011b, 2011c 2012). These values similar to those of the authors mentioned above make the films suitable for solar fabrication

Section 6:

Conclusion and Recommendation

New ternary thin films of iron copper sulphide, iron zinc sulphide, lead silver sulphide, copper silver sulphide and copper zinc sulphide using solution growth technique (SGT) have been grown and characterized. The deposited films were characterized using UNICO-UV-2102 PC Spectrophotometer and Olympus PMG which showed that the films have crystal structure.

The following properties were studied: absorbance, transmittance, reflectance, absorption coefficient, refractive index, extinction coefficient, optical conductivity, thickness, band gap energy, and dielectric constant.

The spectral analysis revealed that FeCuS, FeZnS, PbAgS, CuAgS and CuZnS films have high absorbance in the UV-region and low absorbance in the VIS-NIR-regions. They have low transmittance in the UV-region and high transmittance in the VIS-NIR-regions. FeCuS, FeZnS, CuAgS and CuZnS films have high reflectance in the UV-region and low reflectance in the VIS-NIR-regions, while PbAgS film has low reflectance in UV-region and high reflectance in the VIS-NIR-regions.

The other optical and solid state properties revealed that (1) FeCuS films have absorption coefficient (α) ranging from 0.1×10^6 to $1.6 \times 10^6 \text{m}^{-1}$, while the refractive index (n) ranged from 1.2 to 2.3. The optical conductivity (σ_o) ranged from $0.03 \times 10^{14} \text{s}^{-1}$ to $0.6 \times 10^{14} \text{s}^{-1}$, while the extinction coefficient (k) ranged from 0.005 to 0.038. The direct band gap (E_g) ranged from 2.4eV to 2.8eV and the indirect band gap (E_g) ranged from 0.6eV to 1.0eV, while the real and imaginary

parts of the dielectric constant (ε) ranged from 1.4 to 5.2 and 0.008 to 0.136 respectively. The thickness (t) ranged from 0.0103μm to 0.873μm.

FeZnS films have absorption coefficient (α) ranging from $0.2 \times 10^6 m^{-1}$, while the refractive index ranged from 0.72 to 2.3. The optical conductivity (σ_o) ranged from $0.07 \times 10^{14} s^{-1}$ to $0.6 \times 10^{14} s^{-1}$ while the extinction coefficient (k) ranged from 0.004 to 0.056. The direct and indirect band gap energy (E_g) were 2.9eV and 1.9eV respectively, while the real and imaginary part of the dielectric constant (ε) ranged from 0.7 to 5.2 and 0.008 to 0.164 respectively. The thickness (t) ranged from 0.0899μm to 1.25μm.

PbAgS films have absorption coefficient (α) ranging from $0.5 \times 10^6 m^{-1}$ to $0.9 \times 10^6 m^{-1}$, while the refractive index ranged from 0.1 to 2.3. The optical conductivity (σ_o) ranged from $0.06 \times 10^{14} s^{-1}$ to $0.6 \times 10^{14} s^{-1}$, while the extinction coefficient (k) ranged from 0.010 to 0.140. The direct and indirect band gap energy (E_g) ranged from 1.5eV to 2.1eV and 0.3eV to 0.8eV respectively, while the real and imaginary parts of the dielectric constant (ε) ranged from 0.4 to 5.2 and 0.010 to 0.390 respectively. The thickness (t) ranged from 0.0103μm to 0.873μm.

CuAgS films have absorption coefficient (α) ranging from $0.5 \times 10^6 m^{-1}$ to $1.28 \times 10^6 m^{-1}$, while the refractive index (n) ranged from 1.94 to 2.28. The optical conductivity ((σ_o) ranged from $0.24 \times 10^{14} s^{-1}$ to $0.6 \times 10^{14} s^{-1}$, while the extinction coefficient (k) ranged from 0.025 to 0.064. The direct and indirect band gap energy (E_g) were 2.3eV and 1.1eV respectively, while the real and imaginary parts of the dielectric constant (ε) ranged from 3.8 to 5.2 and 0.100 to 0.290 respectively. The thickness (t) ranged from 0.0103μm to 0.592μm.

CuZnS films have absorption coefficient (σ_o) ranging from $0.24 \times 10^6 m^{-1}$ to $1.6 \times 10^6 m^{-1}$, while the refractive index (n) ranged from 1.6 to 2.3. The optical conductivity (σ_o) ranged from $0.12 \times 10^{14} s^{-1}$ to $0.6 \times 10^{14} s^{-1}$, while the extinction

coefficient (k) ranged from 0.008 to 0.082. The direct and indirect band gap energy (E_g) ranged from 2.2eV to 2.4eV and 0.4eV to 0.9eV respectively. The thickness ranged from 0.048μm to 0.627μm.

From these results, it was observed that the films have the property of screening off UV portion of the electromagnetic radiation by absorbing and reflecting and the admittance of the visible and infrared radiation by transmission. These properties confirm the films good materials for coating poultry buildings, eye glasses coating, solar thermal conversion, solar control, anti-reflection coating and solar cells fabrication. Comparing the maximum absorption coefficient of the five films grown, it was observed that FeZnS has the highest value followed by FeCuS, CuZnS, CuAgS and PbAgS in that order. While the maximum refractive index of the films is of the same value of 2.3 except for CuAgS with value of 2.28. The maximum value of the optical conductivity for the films is the same. PbAgS films has the highest value of extinction coefficient followed by CuZnS, CuAgS, FeZnS and FeCuS in that order. While the maximum value of 5.2 for the real part of the dielectric constant are the same for all the films. The values of band gap energy, imaginary part of dielectric constant and thickness vary from one film to another. We believe that the similarities are due to the fact that the same substrate (glass) was used for the growing of the films.

The films were found to be photo-conducting with voltage ranging from 0.1mV to 0.6mV inside the room and 0.6mV to 15mV outside the room around 9.30 am.

The various films grown in this work could be used in the following areas:

(a)   In agricultural industry such as greenhouse effect,
(b)   In car industry such as anti-dazzling on the windscreen,
(c)   In electronics industry such as in camera lens and coating of eye glasses and
(d)   in architectural industry such as poultry house and coating of windows and doors for passive heating and cooling.

The method of growing thin films may be similar all over the scientific world but the films grown are different. This work was based on growing new sets of thin films of different substances using solution growth technique (SGT).

Recommendation

1   It is recommended that other methods of deposition such as physical vapour deposition (sputtering) etc should be used. The result obtained will be compared with the results of this work

2   Testing of new combinations of semi-conducting materials and electrolyte-solvent systems

3   Using other types of substrates such as metals etc

4   Assembling of the solar cells into modules

5   Development of assembling technologies

6   Using concentration greater than 0.5mole for the various materials used

7   To look into the possibility of using other group III –VIII elements for thin film growth

8   To look into the possibility of coating the windows and doors for passive cooling.

Section 7:

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- My In-laws
- My friend, roommate, sister, soul mate, spiritual power house, the love of my life, my beloved in whom I am well pleased and my wife Stella Ihuoma Uhuegbu
- Our lovely children God made us caretaker over- Chukwuemeka, Kosisochi and Chioma Uhuegbu
- And my two friends who would have been over excited to be here today my father late Mr. Samuel O. Uhuegbu and My Ph.D Supervisor late Professor Elisha B. Babatunde.
  Chairman Sir, I am still a work in progress whose end product is unknown except to the workman who is God,

This is the INAUGURAL .... I can now SIT .

May the good Lord preserve and keep you all for listening. Amen.

Section 8:

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