

Chemical Bath Deposition Technique of Thin Films: A Review



Physics

KEYWORDS : Chemical Bath Deposition (CBD), Chalcogenide, Thin Films, Complexant

| | |
|----------------------|--|
| B. A. Ezekoye | Department of Physics and Astronomy, University of Nigeria. |
| P.O. Offor | Department of Metallurgical and Materials Engineering, University of Nigeria |
| V. A. Ezekoye | Department of Physics and Astronomy, University of Nigeria. |
| F. I. Ezema | Department of Physics and Astronomy, University of Nigeria. |

ABSTRACT

This paper critically reviewed the chemical bath deposition (CBD) method of thin film syntheses as well as the theories of early growth (nucleation) mechanisms of growth into continuous films and characterizations of the synthesized thin films using state-of-art techniques such as energy dispersive X-ray Spectrometry (EDS), Scanning electron microscopy (SEM), tunneling electron microscopy (TEM), X-ray diffraction (XRD) and UV-VIS Spectrophotometer. The films deposited by this technique have possible applications in anti-reflection, anti-dazzling, thermal control widow coatings, optical filters, total reflectors, poultry protection and warming coatings, light emitting diodes, solar cell fabrication and varistors.

1.0 Introduction

There are many techniques available in the recent times used by researchers in the deposition of thin films of different materials on substrates or on previously deposited layers (Bode, 1963). These techniques are categorized into three namely thermal evaporation, sputtering and chemical deposition (Bode, 1966). Chemical bath deposition (CBD) belongs to the third group and is of greater commercial value than either thermal evaporation or sputtering and has attracted the attention of researchers today due to its simplicity, convenience, replicability, large area scaling and commercial production (Bode, 1966).

The solution growth technique was pioneered by the works of Bode and co-workers at Santa Barbara Research Centre, Kitaev and co-workers at Ural polytechnic (Kitaev & Terekhova, 1970), and Chopra and co-workers at the Indian Institute of Technology, Delhi, India (Chopra and Das, 1983). The technique itself was first used in 1946 to prepare PbS films for infrared applications. However, it is only recently that large-area and large-scale applications of these techniques to obtain doped and undoped multi-component semiconductor films of usual, unusual and metastable structures have necessitated an understanding of the physics and chemistry of the processes involved (Chopra and Das, 1983).

Since the mid-1970s, and accelerating significantly in the 1990s, techniques for depositing oxide thin films from aqueous solutions at low temperature (<100°C) have been reported in literatures. Such approaches offer a variety of technological and environmental advantages over alternative routes to depositing films, as described in recent reviews (Niesen, 2001). Chemical Bath Deposition technique has been used extensively for the deposition of sulphides and selenides, oxides, and ternary compound (Eze & Okeke, 1997; Ndukwe, 1992). The choice of this method arises from its low cost, ease of handling, possibility of application on a large surface, and simplicity of instruments for deposition (Ndukwe, 1992). Hence it is most suitable for adaptation in developing countries where facilities for other highly expensive and technically advanced techniques such as Chemical Vapour Deposition, Spray Pyrolysis, Electrochemical Deposition, Molecular Beam Epitaxy, RF Sputtering, Vacuum Evaporation, Pulse Laser, etc. are not easy to come by (Chopra and Das, 1983). Chemical bath deposition technique offers a means of intensively producing large area sample, utilizing a technology readily adaptable to industrial production. The properties of the deposited material can be varied and controlled by proper optimization of the chemical baths and deposition conditions (Ndukwe, 1992; Ezema and Okeke, 2003; Ezekoye, Okeke, 2005; Agbo and Ezema, 2007).

Various methods of preparing thin films include spray pyrolysis, vacuum evaporation, electrodeposition, screen printing, chem-

ical vapour deposition, RF sputtering and chemical Bath Deposition (CBD) or solution growth technique (SGT). However, there are some problems associated with each of the techniques. For example it is difficult to obtain good stoichiometry by evaporation technique and for spray pyrolysis as high temperature is needed. Some of the films produced by some of the techniques have the problems of either thermal loss and/or loss of visible transmittance, coupled with problems of production method, which may not allow large area processing and low fabrication cost. Solution growth techniques, allows deposition of thin films with few defects. Chemical solution deposition technique is a relatively inexpensive, simple thin film process that is able to produce stoichiometrically accurate crystalline phases (Nair & Nair, 1987; Ezema & Okeke, 2002).

2.0 Physical Aspects

A liquid precursor (reacting solution) undergoes a chemical change at a solid (substrate) surface, leaving a solid layer (thin film). The substrates were normally cleaned (washed, scrubbed, degreased, rinsed) and dried, other equipment used were also cleaned alongside with the substrates following the same procedure (Ezema, 2005; Ugwu and Onah, 2007).

A simple procedure adopted for cleaning the substrate is as follows: scrubbing thoroughly with liquid detergent for 10 minutes; rinsing several times with distilled water; scrubbing again with detergent for 5 minutes; rinsing again with distilled water; scrubbing for 5 minutes with trichloromethylene; scrubbing for 5 minutes with acetone; scrubbing for 5 minutes with alcohol; rinsing with distilled water; and lastly, drying in oven or a hot plate for 5 minutes using a heat gun.

The cleaning process etches the surface of the substrate to form nucleation sites, which aids proper adhesion of the thin films to the substrate surface during deposition. Various Researchers used different clearing agents. Examples include degreasing in HNO₃, HNO₃ and HCL (Ezema, 2005), ultrasonic bath with acetone and a water-ethanol (50:50) solution. The degreasing time varies from 5-48 hours. The methods of drying the cleaned substrates also varied dry in air, drying in oven or a hot plate. Others did not indicate the drying agent and/or method of drying employed. Micro-glass slides could first be cleaned in chromic acid, followed by repeated washing in deionized water as Successive Ionic Layer Adsorption and Reaction (SILAR) method (Ezema, 2005).

To deposit thin films on substrates by the chemical bath method, volume(s) of the chemical bath solution is prepared. The resulting solution is well stirred and the substrate, which was previously degreased, is clamped vertically into the solution inside a beaker with synthetic foam in order to prevent dust or unwanted particles from entering into the solution. The solution

is prepared into several beakers and left for the required dip times, (with dip times ranging from 6-72 hours) at the deposition temperatures (Ezema, 2005).

3.0 Chemical Aspects

A thin film deposition process involved threestep:(i) creation of atomic/molecular/ionic species, (ii) transport of these species through a medium, and (iii) condensation of the species. The basic principle involved in the synthesis of thin films by the chemical bath method is the controlled precipitation of the desired compound from a solution of its constituents. The ionic product must exceed the solubility product, thus the formation of thin films on substrates by ion-by-ion condensation (Chopra & Das, 1983). Deposition medium for chemical bath consists of one or more salts of metal M^{n+} , a source for the chalcogenide X (X = O, S, Se), and usually a complexing agent (e.g. ammonia,), in aqueous solution (Niesen, 2001; Niesen & De Guire, 2002. Examples of chelogenide sources include: thiourea ((N_2H_4) CS) for sulphide ions (S^{2-}) and selenourea ((N_2H_4)CSe) for for selenoure ion (Se^{2-}) while the water itself provides oxygen, initially in the form of hydroxide ions (OH^-). Generally, the processes or steps involved in the Chemical Bath Deposition are as follows (Niesen & De Guire, 2002):

Equilibrium between the complexing agent and water;

Hydrolysis of the chalcogenide source;

Formation/dissolution of ionic metal-ligand complexes $[M(L)_i]^{n-i}k$, where L^k denotes one or more ligands.

The reaction (Natalia, Frank and Andreas, 2009):



Can be written as

$$C_{m,o} [M^{2+}] \left[1 + \beta_1 [L] + \beta_{1,2} [L]^2 + \dots + \beta_{1,2,\dots,n} [L]^n \right] \tag{2}$$

where $C_{m,o}$ and L are the total metal and free ligand (complexing or chelating agent) concentrations, respectively, $[M^{2+}]$ is the free metal ion concentration and β is the cumulative thermodynamic formation constant.

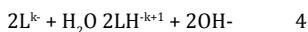
The RHS term,

$$\beta_{1,2,\dots,n} = \left[\frac{ML_n^{2+}}{M^{2+}} \right] [L]^n \tag{3}$$

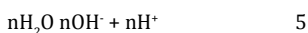
3.1 Reactions in Chemical Bath

As applied to chemical Bath Deposition of oxide films from a metal cation $Mn+$ complexed by i ligands $Lk-$, these steps can be formulated as follows (Eze & Okeke, 1997; Natalia et al. 2009):

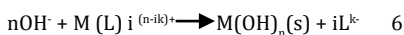
complexant- H_2O equilibrium:



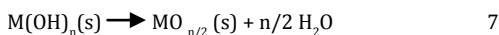
dissociation of water:



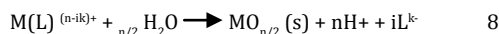
displacment of ligands:



deprotonation to form oxide:



Net reaction:



The complexant, when listed, is usually chosen for the affinity of its ligands toward the metal. The complexant (complexing agent or ligand) as a component of the bath eliminates spontaneous precipitation by slowing down the release of the metallic ions on dissociation thereby resulting in slow precipitation of the compound (Chopra and Das, 1983) . This could make 4 step 3 the rate determining step, thus slowing down (and therefore providing a degree of control over) the rate of solid formation.

The hydrolytic process depicted by reactions (7) and (8) is sometimes called "forced hydrolysis (Barnes and Czeeny, 1931). It does not require addition of base, even though the hydroxyl ion appears on the left side of reaction (6). It can be accelerated simply by heating the solution, which induces deprotonation of the hydrated metal species (reaction 7). Hydrolysis can occur even in acidic solutions when the metal cation is easily hydrolysable, as with Fe^{3+} , Ti^{4+} , Zr^{4+} , and Al^{3+} . In contrast, chemical Bath Deposition of non-oxides has been carried out almost exclusively in basic solutions.

In all Chemical Bath Deposition processes whether oxide (reaction 8) or non-oxide, a solvated metal complex reacts with a chalcogenide source to form a desired solid product. The main difference is that, for non-oxide films, the supply of chalcogenide anions (and thus the rate of hydrolysis) can be more readily controlled via adjustments in pH, temperature and the concentration of the chalcogenide source. In the Chemical Bath Deposition of oxides, the "chalcogenide source" is water, so that tighter control must be exerted over just two parameters (pH, T) to achieve a similar degree of control over the rate of hydrolysis (and, by implication, control over the films microstructure and properties).

The deposition process involved the reaction of the positive and negative ions to form neutral atoms, which are precipitated as thin films [24] (Chopra and Das, 1983).

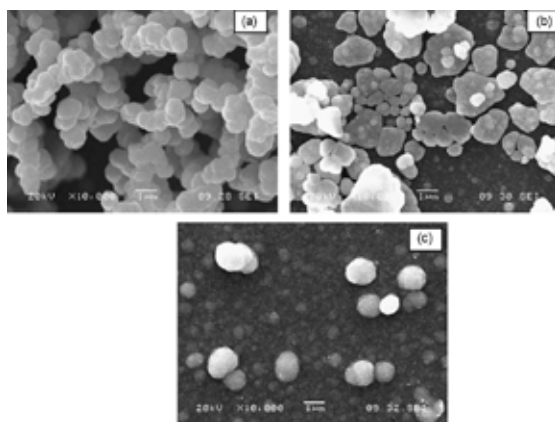
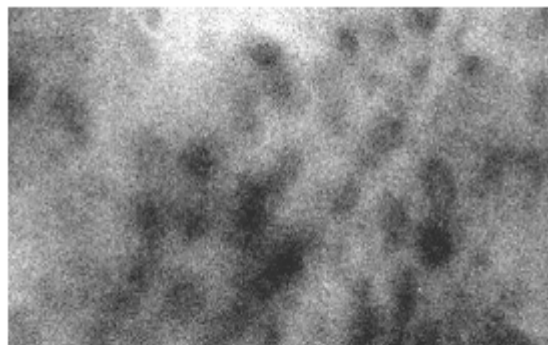


Fig. 1: SEM micrographs for $Bi_{2-x}Sb_xSe_3$ films: (a) $x = 0$, (b) $x = 0.04$, and (c) $x = 0.08$ from Chemical Bath (Patil, Sargar, Maneb, Bhosaleb, 2009).



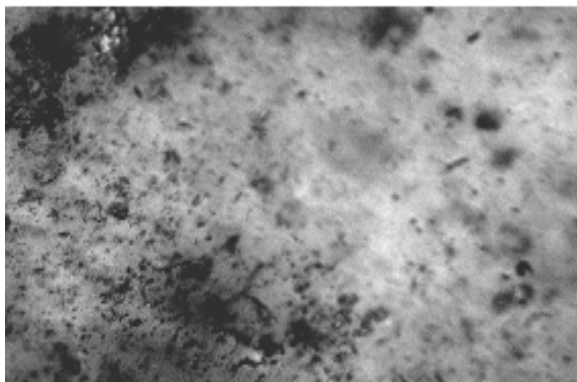


Fig. 2: Optical micrographs of PbS Films from chemical Bath (Oriaku and Osuwa, 2008).

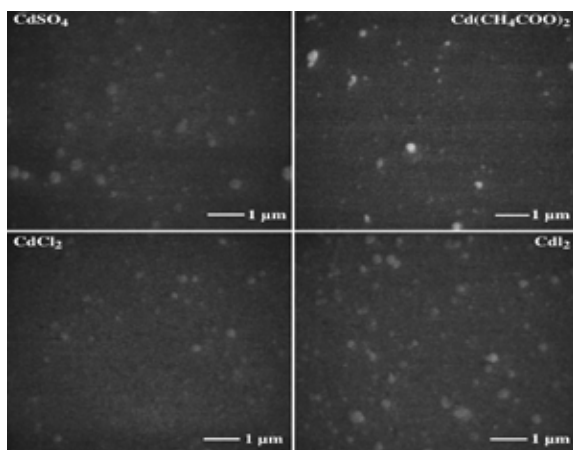


Fig. 3. SEM micrographs of CdS films deposited on quartz using two different Cd sources from chemical bath (Patil et al. 2009).

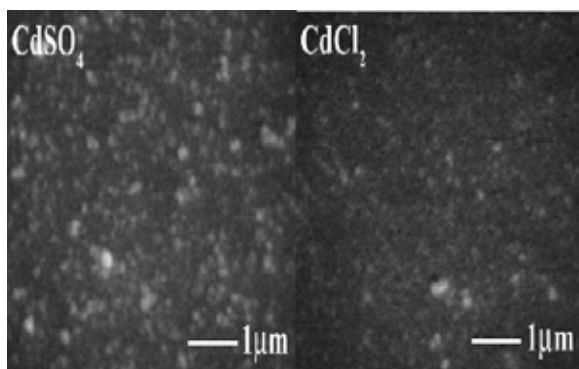


Fig.4: SEM micrograph of CdS films grown using four different Cd sources from chemical bath (Khallaf, Oladeji, Chai, and Chow, 2008).

3.2 Deposition Conditions of Thin Films

The kinetics of growth of a thin film in this process is determined by the ion-by-ion deposition of the chalcogenide on nucleating sites on the immersed surface. Initially, the film growth rate is negligible because an incubation period is required for the formation of critical nuclei from a homogeneous system unto a clean surface. It is necessary to eliminate spontaneous precipitation in order to form a thin film by a controlled ion-by-ion reaction. This can be achieved by using a fairly stable complex of the metal ions which provides a controlled number of the free ions according to an equilibrium reaction. Sparingly soluble salt, AB, when placed in water, a saturated solution containing A^+ and B^- ions in contact with undissolved solid AB is obtained and equilibrium is established between the solid phase and ions in the solutions (Pathan and Lokhande, 2004). The

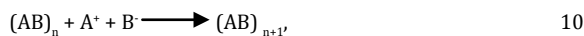
ionic product IP is given by $C_A^+ \cdot C_B^-$ constant (called the solubility product SP, Ks). There is no equilibrium if this relationship is not satisfied¹⁵. If the ionic product exceeds the solubility product, precipitation occurs. Once nucleation occurs the growth rate rises rapidly until the rate of deposition equals the rate of dissolution i.e. $IP = SP$. Consequently the film attains a terminal thickness. When $IP < SP$, the solid phase will dissolve until the above relation is satisfied.

The rate of formation of nuclei on the surface of the substrate depends on the degree of supersaturation. The formation of suitable growth centers on the surface, $N(t)$, can be expressed as a function of total number of active sites on the surface, N_0 , by the law:

$$N(t) = N_0 \exp(-At) \quad 9$$

where A is nucleation rate constant.

From these stable growth centers, various models have been proposed to describe either bidimensional (monolayer) or three-dimensional growth. Growth of particles, already present in the solution takes place in the second step, when nuclei or other seed particle are present. In case of ionic solids, the process involves deposition of cation and anion on appropriate sites.



where n is the minimum number of A^+ and B^- required for giving stable phase, $(AB)_n$.

Chemical Bath Deposition requires supersaturated solutions, that is, the product of the concentrations of metal and chalcogenide must exceed the solubility product of the desired solid. In a closed system growth cannot continue once the reactants obtainable thickness is limited by the supply of reactants (Niesen, 2001). Increasing the degree of supersaturation (for example by raising the pH, in the case of oxides) increases the rate of film growth, as reported by several groups (Chopra and Das, 1983; Nair and Nair, 1989) under such conditions of rapid formation of solid, however, some of the solid forms powder, or relatively large particles that are only weakly adsorbed to the film. Thus, the films thickness is less than would be expected based on maximum utilization of the reactants. Solutions that are less heavily super saturated grow more slowly but ultimately provide thicker films-“a tortoise and hare” effect [18] (Niesen, 2001).

Several workers (Chopra and Das, 1983; Nair and Nair, 1989) have reported the effect of varying growth parameters such as deposition rate, bath composition and bath temperature on the various properties of their films. On a presensitized substrate surface, no incubation period for nucleation is observed, since nucleation centers already exist on the substrate. Also, when the substrates are suspended in the container before forming the complex in the solution, film thickness increases in a manner similar to that of the sensitized surface, thereby showing that the nuclei for the formation of the film are provided by the solution itself. If a change in metals' oxidation state occurs, it takes place in the bulk solution (Niesen, 2001). The rate of deposition and the terminal thickness both depend on the number of the nucleation centers, super saturation of the solution (defined as the ratio of IP to SP), and stirring. The growth kinetics depend on the concentration of ions, their velocities, nucleation and growth processes on the immersed surfaces¹⁵.

4.0 Characterizations of the Films

4.1 Thickness of the thin films: The film thickness is obtained using different methods as surface profiler, gravimetric method, etc. When the film is deposited on only side of the substrate, the film thickness t is given by [65] (Oriaku and Osuwa, 2008):

$$t = \frac{m}{\rho A}, \tag{12}$$

where m is the mass of the deposited film measured with a very sensitive electronic balance, A is the area in cm^2 and ρ is the density of the film obtained from crystallographic data.

4.2 X-ray Diffraction (XRD)

The grain size of the crystallite is obtained by substituting values of Full Wave Half Maximum (FWHM) in the well-known Debye-Scherrer formula (Ezema & Okeke, 2003):

$$D = \left(\frac{K\lambda}{\beta \cos \theta} \right) \tag{13}$$

where D is grain size of the crystallite, $K = 0.94$, λ ($=1.54059 \text{ \AA}$) is the wavelength of the X-ray source used, β is the broadening of the diffraction line measured at half of its maximum intensity in radians (FWHM) and θ is the angle of diffraction at the peak.

4.3 Optical Characterizations

A) Absorbance of the Film: The optical information is obtained using spectrophotometer. The absorbance A is obtained from the relation:

$$\alpha = \left[\left(\frac{2.30A}{t} \right) \right] \tag{14}$$

where t is the thickness of the deposited film, A is the absorbance and reflectance is neglected for highly transmitting film.

B) Bandgap Estimation: The bandgap of materials is a very important parameter that determines the application of the films. It is evaluated using the formula (Ezekoye & Okeke, 2005).

$$\alpha = \left(\frac{A}{h\nu} \right) (h\nu - E_g)^n \tag{15}$$

where $n = 1/2, 2, 2/3, 3$ for allowed direct and indirect and forbidden direct and indirect transitions.

For direct bandgap materials, $n = 1/2$, and $n = 2$ for indirect bandgap materials. The plot of α^2 or $(ah\nu)^2$ versus photon energy, $h\nu$ (in electron volts) with extrapolation of the straight line portion of the curve to zero absorption coefficient ($h\nu$ axis) gives the bandgap energy for direct bandgap materials. The plot of $\alpha^{1/2}$ or $(ah\nu)^{1/2}$ versus photon energy $h\nu$ (in electron volts) with extrapolation to zero absorption coefficient ($h\nu$ axis) gives the bandgap energy for indirect bandgap materials (Ezekoye & Okeke, 2005).

5.0 Application of Thin Films Prepared by Chemical Bath Deposition

Some of the films were found to have very high absorbance in UV-VIS-NIR regions while the films absorbance increased as the thickness increased hence they could find applications in solar radiation absorbers for solar cell applications²⁵. The properties of high transmittance throughout UV-VIS-NIR make the film good materials poor for the thermal control window coatings for cold climates and antireflection coatings, moderate transmittance make the film good material for antidazzle coating windscreen of a car while transmittance make the film good materials for solar cell absorber. It is observed that as the deep time increases, the absorbing power of the film increases, hence the

film move from poor absorbance to moderate and then reaches heavy absorbance. With the increase in absorbing power the negative absorbance disappears. Transparent films can be used as optical filters, polarizers, total reflectors, narrow pass-band e.t.c. (Sabestian & Hu, 1989). Some films have low absorbance in the UV region, which decreased with increasing wavelength towards the NIR regions. Some film generally exhibited absorbance throughout the UV-VIS-NIR regions. The films show high transmittance in the UV, VIS and IR regions of the electromagnetic spectrum. Conversely, the reflectance of the films is found to be low within the same region. These high transmittance and low reflectance properties make the films good materials for antireflection coatings and for solar thermal applications in flat-plate collectors, house heating for solar chick brooding, etc. (Chopra and Das, 1983) .

The spectral analysis revealed that some of the films grown are poor transmitters of UV but exhibit very good transmission in the VIS-NIR regions. The films have potential applications for poultry protection and warming coatings, solar control and antireflection coatings, solar cell absorbers, thermal control and photosynthetic coatings.

Chemical Bath Deposited films are now being developed to be utilized in converting solar radiations into electricity. The effectiveness of a thin film surface in narrowing the photon energy distribution has been extensively established in literature. The material properties that are of interest for these films are the optical properties within the range of UV, VIS and NIR, which strongly depend on the band-gap of the thin film, and depend very much on the nature of the film materials properties. Other applications of this type of film relate to their use in decorative and protective coatings. These properties determine the absorbance, transmittance, reflectance and optical conductance characteristics of the film. Thus, the study of the solid state properties of the thin film would give one an idea of these characteristics which arise as a result of the interaction between photon energies and the structure of the thin film or between the energy configuration and other optical constants (n and k) of the material. Some films have wide band gap and large break down strength. Some wide gap semiconductors have found applications in light emitting diodes, photodectors, sensors for gas detectors; electrode and piezoelectric devices, varistors, dye sensitized solar cells, surface acoustic wave devices, optoelectronic devices. Films with narrow band gaps are used as solar absorber materials for solar cell fabrication and large area selective coatings for photo thermal conversion of solar energy due to their high absorbance.

6.0 Conclusion

Chemical Bath Deposition (CBD) technique has been severally used for deposition of thin films of different materials. The technique is not new, yet its potential is a challenge to modern day researchers. It is a relatively inexpensive, simple thin film process that is able to produce a stoichiometrically accurate crystalline phases. The properties of the deposited material can be varied and controlled by proper optimization of the chemical baths and deposition conditions. The possible areas of application of the films are based on the optical and solid-state properties of the films. Among others, some of the films could be effective as thermal control window coatings for cold climates and antireflection coatings, which could be used for antidazzle coating for windscreen of cars and solar cell absorbers.

REFERENCE

- Agbo, S. N. and Ezema, F.I. (2007) Pacific J. Sci. Tech. 8 (1), 1-5. | Barnes, R. B. and Czeeny, M. (1931). Phys. Rev. 38:323. | Blatt, F.J. (1968). Physics of electronics conduction in solid. McGraw Hill: New York | Bode, D. E. (1963). Proc. Natl. Elec. Conf. 91, 630 | Bode, D. E. (1966). Physics of Thin Films (3), Academic Press, New York. | Chopra, K. L. and Das, S.R. (1983). Thin film Solar Cells. Plenum Press, New York. | Cox, P.A. (1978). The Electronic structure and chemistry of Solids. Oxford University Press: Oxford. | Dixon, A.E. and Leslie, J.D. (1978). Waterloo, Ontario, Pergamon press, N.Y. | Eze, F. C. Okeke, C.E. (1997). Mater. Chem. Phys., 47 31-36. | Ezekoye, B. A. Okeke, C.E. (2005). Pacific J.Sci. Tech. 6 1 23-38 | Ezema, F. I. Okeke, C. E. (2003). Greenwich J.Sci. Tech. 3 90-109. | Ezema, F. I. and Okeke, C.E. (2002). Nig. Journ. of Physics, 14 (2): 77-85. | Ezema, F. I. (2005). Turk J. Phys. 29, 105-104. | Ezema, F. I. et al. (2007) Journal of the University of Chemical Technology and Metallurgy, 42, 2, 217-222. | Ezeugwu, S. (2008). Unpub. Post Graduate Seminar, University of Nigeria, Nsukka. | Garg, P. Treatise on Solar Energy, Vol. 1, Fundamentals of Solar Energy. Wiley-inter Science Publication, New York | Khallaf, H., Oladeji, I. O. Chow, L. (2008). Thin Solid Films. 516, 5967-5973. | Khallaf, H. Oladeji, I. O., Chai, G., Chow L. (2008). Thin Solid Films. 516, 7306-7312. | Lokhande, C. D. (1991) Mater. Chem. Phys. 271. | Madelung, O. Data in science and Technology: semiconductors other than Group IV and III-V compounds, Springer, New York. | Matyevic, E. (1985). Annu. Rev Mater. Sci. 15:483-516. | Natalia, S. K. Andrey, A. R. Frank, H. Andreas, M. (2009). Thin Solid Films, 517, 2586-2589. | Ndukwe, I.C. (1992). Unpublished Ph. D Thesis University of Nigeria, Nsukka. | Nair, P. K. and Nair, M.K.S. (1987). Sol. Ener. Mater. 15, 431-440. | Nair, P.K and Nair, M.T.S. (1989). Semicond. Sci. Technol. 4:807-811. | Niesen, T.P. and De Guire, M.R. (2002). Solid State Ionics. 151 61-68. | Niesen, T. P. (2001). J. Electroceram. 6, 169-207. | Oriaku, C.I. and Osuwa. J.C. (2008). Pacific Journal of Science and Technology. 9(2) 461-467. | Pathan, H.M and Lokhande, C.D. (2004). J. Bull, Mater. Sc. 27. 85-111. | Patil, N.S. Sargar, A.M. Maneb, S.R. Bhosaleb, P.N. (2009). Materials Chemistry and Physics. 115, 47-51. | Raviendra, D. and Sharma, J.K (1985) J. Appl. Phys. 58, 838-844. | Raviendra D. and Sharma, J.K. (1985) J.Phys. Chem. Solids, 46, 945-950. | Sabastian P.J. and Hu, H. (1989). Adv. Mater. Opt. Electron, 4:407-412. | Tarasevich B.J. and Rieke, P.C. (1996) Chem. Mater. 8, 292-300. | Ugwu, E. Land Onah, D. U. (2007). Pacific Journal of Science and Technology, 8 1 155-161