## CHAPTER-II

<table>
<thead>
<tr>
<th>S. No</th>
<th>Sub title name</th>
<th>Page No</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1.</td>
<td>LITERATURE REVIEW</td>
<td>24</td>
</tr>
<tr>
<td>2.2.</td>
<td>SCOPE OF THE PRESENT WORK</td>
<td>33</td>
</tr>
<tr>
<td>2.3.</td>
<td>OBJECTIVES OF THE PRESENT STUDY</td>
<td>34</td>
</tr>
</tbody>
</table>
2.1. LITERATURE REVIEW

Extensive research has been done on the deposition and characterization of iron pyrite thin films due to its potential applications. Direct and indirect band gap iron sulphide thin films is the subject of intensive research because of its intermediate band gap for the absorber material in solar cells, high absorption coefficient, electron affinity, low resistivity, easy ohmic contacts and finally the structure. The aim of the present work is to highlight the temperature variation, precursor concentration variation, different complexing agents and variation of their concentrations, etc., in the determination of structural, morphological, optical and electrical properties. This section presents an overview of the work both in deposition techniques and different studies of iron pyrite thin films.

K Anuar and his co-workers [47] have deposited FeS$_2$ thin films in aqueous solutions of precursors onto microscopic glass substrates by CBD. They studied structural, morphological and optical properties of the deposited films. These films showed direct band transition. They deposited the films at different pH values and the band gap values were found to be varied from 1.85 eV to 2.25 eV. Their studies
revealed that the film deposited at pH 2.5 had a good crystallinity, surface coverage and band gap energy.

K Anuar et al [51] also studied the effect of deposition period on the properties of FeS$_2$ thin films. The deposited thin films were characterised by XRD, SEM and UV-Vis spectrophotometer. They prepared the films by using iron nitrate and sodium thiosulphate under CBD. This work revealed that the film deposited for 90 min show large grain size and more peaks attributed to FeS$_2$. This work also explains that the band gap energy decreased from 2.65 eV to 1.85 eV as the deposition time increased from 30 min to 90 min.

Prabhukanthan et al [52] deposited iron-sulfur thin films onto soda lime glass substrates by using chemical deposition method at low temperature. The aqueous solutions of ferrous sulphate, di-sodium salt of ethylenediamine tetraacetic acid, sodium thiosulphate and organic solutions of ethylenediamine and methanol were used as bath. The experiment was performed at room temperature and at two different conditions. The deposited films were uniform and adhered well to the substrates. The as-deposited and annealed thin films were characterised by XRD, SEM, Optical absorption and Auger electron spectroscopy. During this work, cubic phase pyrite thin films having good crystallinity were synthesized by two CBD techniques. They reported that the pyrite cubic phase and optical band gap are controlled by the disorder in the film’s network regardless of the sulfurization temperature and time duration. They investigated that Ni
as an inexpensive ohmic contact makes pyrite films promising material for photovoltaic applications.

Shuling Liu et al [48] synthesized FeS$_2$ thin films by the solvothermal method using potassium ferrocyanide as Fe source and sulphur powder as S source in the presence of Polyvinyl Pyrrolidone (PVP). Their work represents the phase and morphology of the products by means of XRD and SEM. They found that solvent ratio and temperature play a crucial role in the formation of FeS$_2$ with cubic structure. The phase and purity of the products were analysed. This report concluded that the degradation efficiencies of the as-deposited pyrite FeS$_2$ crystallites for some typical dice can reach their expectation after the integrated effect of several compositions.

Nicholas Berry et al [49] prepared iron pyrite thin films by the method of Atmospheric pressure chemical vapour deposition. In this report, single phase large grain and uniform polycrystalline pyrite thin films are fabricated on glass substrates. They found that the pyrite-marcasite phase composition depends strongly on the concentration of sodium in the glass substrate and the sulphur partial pressure during annealing. The prepared films were characterised by XRD, Raman, AES, etc. They concluded that CVD pyrite thin films were well suited in fundamental electrical studies and the fabrication of pyrite photovoltaic device stacks.

Swaroop Kumar Mazi et al [50] fabricated nanocrystalline FeS thin films on fluorine doped Tin oxide coated glass substrate by the thermal decomposition of a precursor complex in aqueous solution.
This work revealed that FeS films also been used as an amperometric sensor for the detection of $\text{H}_2\text{O}_2$ and found to have a rapid response time. The results indicate that the FeS thin film was a good nanostructured material for potential applications in photoelectrochemical solar cells, fuel cells and sensor constructions.

Masood Akthar et al [53] from the University of Manchester prepared iron sulphide thin films by the Aerosol Assisted Chemical Vapour Deposition (AACVD) method. They used unsymmetrical and symmetrical iron complexes as single source precursors for the deposition of the iron pyrite thin films. They found that the pyrite phase was dominant in all samples deposited from the unsymmetrical complexes, whereas, the pyrrhotite phase was dominant in samples deposited from symmetrical complexes.

Z J Luan and his co-workers [54] prepared iron pyrite films by sulfurizing the precursive films at different temperatures. The microstructure, chemical compositions and surface free energy had been investigated. The results indicated that pyrite films were obtained after sulfurization process of the precursive films. The authors found that the surface free energy is significantly depends on the sulfurization temperature and chemical composition of the films. A possible relationship between the surface free energy and film quality had been discussed.

A J Clayton et al [55] synthesized p-i-n structure pyrite by Metal-Organic Chemical Vapour Deposition (MOCVD) method. Their work revealed the presence of pyrite and marcasite phases of iron
disulphide. Also, they observed that the device with sulfurized FeS$_2$
layers performed least efficiently as a p-n device, even though
fractions of pyrite were present.

J Oertel and his co-workers [56] fabricated n-type
polycrystalline pyrite thin films by MOCVD method. In the present
work polycrystalline pyrite films can be doped in situ with cobalt from
the precursor tricarbonyl-nitrosyl-cobalt. The dopant cobalt leads to
n-type conductivity of the films. With increasing cobalt doping, the
films showed a turn over from p-type to n-type conductivity.

L Y Huange and L Meng [57] studied the effects of film thickness
on microstructure and electrical properties of pyrite thin films. They
prepared the films with thickness in the range of 70-600 nm by
sulfurizing iron films at 673K. They observed that with the increasing
thickness the crystallite size decreased and tend to maintain constant
at film thickness over 300 nm. The conductivity of the film was
maximum at 130 nm thickness and decreases with increase of film
thickness. They observed that carrier mobility increases with
increasing thickness from 70-300 nm and decreases as the film
thickness is greater than 300 nm. The changes of density of crystal
defects, level of face transformation and integrity of the film were
considered to be responsible for the change of electrical properties
with film thickness.

J R Ares, A Pascual, I J Ferrer and C Sanchez [58] fabricated
pyrite thin films by sulfurizing the Fe films which were obtained from
thermal evaporation. The influence of temperature and time of
sulfurization on crystal size and grain size were determined by XRD and AFM. They found that the experimental conditions used to grow the films drastically influence both the parameters. They stated that the physical properties of the films were related to grains or crystallites.

Soumitra Kar and Subhadhra Chaudhury [59] synthesized nano crystalline FeS$_2$ in large quantities by solvothermal process at relatively low temperature. They found that the anions of the iron source, temperature and molar concentrations of the precursors play an important role in controlling the morphology of the FeS$_2$ nano structures. The effects of these parameters have been investigated by SEM and TEM images and also crystal structure was studied by XRD, HRTEM and SAED methods. They concluded that Iron nitrate as precursor favours uniform FeS$_2$ nano wires growth.

A Yamamoto et al [60] prepared pyrite FeS$_2$ thin films by spray method using FeSO$_4$ and [NH$_4$]$_2$S$_x$ as precursors for Fe and S respectively. They observed that although Fe-S compounds including pyrite were formed on the substrate by spraying, sulfurization converts other phases of FeS$_2$ into pyrite. They suggested that the best electrical properties were shown by the films under this method of preparation. They reported that the use of a low concentration FeSO$_4$ solution was found to enhance not only the grain growth of pyrite but also improves its electrical properties.

S Nakamura and A Yamamoto [61] deposited iron pyrite thin films for photovoltaic cells using electrodeposition method using
aqueous solutions of FeSO$_4$ and Na$_2$S$_2$O$_3$. The XPS measurements were carried out to investigate the structural properties of the films. XPS results revealed that this method produced FeS. They concluded that pyrite thin films prepared by this method probably requires S$_2^{2-}$ ion in the solution.

B Thomas et al [62] synthesized pyrite FeS$_2$ thin films on to natural FeS$_2$ and synthetic ZnS crystals by low pressure MOCVD method. Iron pentacarbonyl and di-tertiary butyldisulphide were used as the precursors. The studies revealed that pyrite films can be epitaxially deposited on to natural FeS$_2$ crystals at 475$^\circ$ C. The XRD and RBS studies proved that crystallinity of these epitaxial films was good. Also, they noted that hetero epitaxial film growth on ZnS crystals was not possible at this temperature even at very low deposition rates. The transient microwave conductivity of pyrite films on ZnS substrates proved the role of grain size for photo activity of the pyrite thin films.

M Bronald et al [63] fabricated the polycrystalline pyrite films by molecular beam deposition method using evaporation of Fe and S from separate molecular beam sources on to Mo foil and glass substrates. It was shown that the sulphur pressure is a crucial parameter and larger substrate temperatures are needed for high crystalline pyrite films.

H Dahman, M Khaleefa, M Brunel and B Rezig [64] deposited iron pyrite thin films by sulphur vapour transport. Iron films were obtained by thermal evaporation with a thickness of 100 and 250 nm
and then they were converted into pyrite by open sulphur vapour transport using nitrogen as a gas vector. They obtained pure and homogeneous FeS$_2$ films with high absorbing properties. The authors identified the optical transitions i.e. direct and indirect transitions of iron pyrite.

Kaiwen Sun et al [65] synthesized pyrite FeS$_2$ thin films by sulfurizing oxide precursor films deposited via successive ionic layer absorption and reaction method. The formation mechanism of the pyrite was identified by X-ray photo electron spectroscopy. In the present work Fe$_2$O$_3$ is used as the precursor thin film. The optical and electrical properties were studied by means of Shimadzu UV-3600 spectrophotometer and hot point probe, respectively. They observed that all peaks correspond to pyrite after sulfurization show good crystallinity which was observed by XRD studies. The optical and electrical measurements show that the pyrite films had high absorption coefficient, suitable band gap, p-type conductivity and good photo-electrical conversion capability.

C W Lin and his co workers [66] prepared pyrite FeS$_2$ nano crystals by wet solution phase chemical synthesis method. They studied the efficiency of solar cells by incorporating a small amount of semiconductor FeS$_2$ nano crystals with structure ITO/P3HT: PCBM: FeS$_2$. The current density –voltage (J-V) measurements of the solar cell were made under an illumination intensity of 100mW/cm$^2$. They concluded that pyrite nano crystals enhance the efficiency of the solar cell.
Y H Liu et al [67] fabricated pyrite thin films by annealing the iron films. The structural, optical and electrical characteristics were investigated at different thicknesses of the pyrite films. The observations revealed that the absorption edges changed in range of 0.93-1.0 eV with different thickness by sulfurizing the iron films at 673 K, and films completely converted into pyrite phase. This work revealed that with increasing film thickness the electrical resistivity increases from 0.08 to 0.52 Ω-cm and the carrier concentration decreased from 2.1x10^{20} to 1.66x10^{19} cm^{-3}.

Yu Bi and his co workers [68] reported the rational synthesis of phase pure, highly crystalline and cubic FeS\textsubscript{2} nano crystals using a trioctylphosphine oxide (TOPO) assisted hot-injection method. They observed that the synthesize pyrite NC films have excellent air stability. With TOPO the pyrite nano crystals show good optoelectronic properties for efficient photovoltaic application. They summarized that the FeS\textsubscript{2} NCs have uniform phase pure and air stability.

Sean Seefeld and co workers [69] synthesized pyrite thin films from an iron (III) acetylacetonate molecular ink. Phase and elemental composition of the films were studied by synchrotron XRD, Raman spectroscopy, FTIR spectrometer etc. This work suggests that a common defect or hole-rich surface layer governs the electrical properties of iron pyrite thin films.

Feng Wang et al [70] fabricated the pyrite FeS\textsubscript{2} films by sol-gel method. The structural and photoelectrical characteristics were studied at different sulfurization temperatures. They reported that the
RMS roughness decreases with increase in temperature from 300° to 400° C and then increases above 400° C. The optical absorption coefficient and band gap decrease while the electrical resistivity increases with the temperature. They concluded that the changes of electrical resistivity were more significantly influenced by the changes of carrier concentration.

Paul O Brien and his co workers [71] synthesized iron sulphide thin films from single source precursors by Aerosol-Assisted CVD (AACVD) using dialkyl-dithiocarbamato iron (III) complexes as precursors. The XRD patterns of the films indicated the crystallinity of iron sulphide grown between 375- 450° C. The SEM images revealed that the films grown at lower temperatures form hexagonal phases and higher temperature films tended to form various morphologies.

V G Bessergenev et al [72] prepared iron sulphide, cobalt sulphide and manganese sulphide thin films by CVD. From the GIXRD, LIMS and CEMS results they recommended that pyrite thin films are useful for the production of future solar cells.

2.2. SCOPE OF THE PRESENT WORK

Iron pyrite is a naturally abundant and non-toxic photovoltaic material that can potentially make the devices as efficient as silicon based devices. The literature survey on iron pyrite revealed that much attention was focussed on the preparation and characterization of pyrite thin films using the growth techniques such as thermal evaporation, spray pyrolysis, chemical vapour deposition, molecular beam deposition, sol-gel, pulsed laser deposition, electro deposition.
However, not much work has been done on the preparation of iron pyrite thin films by the chemical bath deposition method. In the present study, chemical bath deposition is employed for the preparation of iron pyrite thin films. It is a relatively inexpensive, simple and convenient method. The physical properties of the films formed depend on the deposition technique used and variants of the deposition conditions. The main advantages of this chemical bath deposition method are large area deposition and control on the physical properties and chemical composition of the films by varying the deposition conditions. Generally, Triethanol Amine (TEA), Ethylene Diamine TetraAcetic Acid (EDTA) are used as the complexing agents. It is an advantage to use ammonia along with EDTA as a novel complexing agent to overcome the commonly noticed problems in CBD like non-uniformity and poor adhesion. In the present investigation, chemical bath deposition technique is employed for the preparation of iron pyrite thin films using ammonia and EDTA as complexing agents for the first time. The deposited films are characterized by appropriate techniques to evaluate their physical properties.

2.3. OBJECTIVES OF THE PRESENT STUDY

The main objectives of the present investigation are the following.

- Deposition of iron pyrite thin films by chemical bath deposition technique by varying
  - Bath temperature
  - Iron precursor concentration
• Complexing agents and
• Concentration of the complexing agents.

❖ Characterization of the as-deposited films to investigate
  ▪ Crystal structure by X-Ray Diffraction and Raman spectrometer
  ▪ Surface morphology by Scanning Electron Microscope, and elemental composition using Energy Dispersive Analysis of X-rays.
  ▪ Chemical binding configuration by Fourier Transform Infrared Spectroscopy
  ▪ Optical studies by spectrophotometric methods and
  ▪ Electrical properties using Hot probe method and Four Probe setup

❖ Investigation of the influence of the deposition parameters on the properties of iron pyrite films to optimize the deposition conditions.