Electrical charge transport and optical properties of iron pyrite

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NANYANG
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**ELECTRICAL CHARGE TRANSPORT AND
OPTICAL PROPERTIES OF IRON PYRITE**

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A thesis submitted to the Nanyang Technological
University in partial fulfilment of the requirement for
the degree of
Doctor of Philosophy

2016

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

14-09-2016

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A handwritten signature in black ink, reading "S. Shukla.", with a horizontal line drawn underneath the name.

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Sudhanshu Shukla

Abstract

Iron pyrite is among the promising solar materials for terawatt scale solar energy conversion owing to its remarkably high optical absorption, optimal band gap, abundance and non-toxicity. However, its solar power conversion efficiency is limited to about 3 % mainly due to its low photovoltage. Despite numerous research efforts, the underlying reasons are still unclear. Researchers attribute this to intrinsic defects, phase impurities and surface problems, in passing, but no one seems to have addressed this issue comprehensively, nor obtained experimental evidence to pin point the root cause. This work builds on the understanding of the subject developed over the decades and explores the problem systematically, in an attempt to find answers, or at least reliable pointers.

The theme of the project is to prepare pyrite thin films of differing microstructures by different fabrication methods to generate films with a variety of defect population, and correlate their impact on optical and electronic properties. The range of samples generated provided an excellent platform to investigate defect physics in pyrite thin films. Thin films prepared by spray pyrolysis, spin-coating of hot-injection synthesized nanocubes and pulsed laser deposition were sulfurized to obtain the pure pyrite phase. They were all p-type and showed similar electrical properties such as high carrier concentration, low mobility and degenerate semiconducting behavior. Their band gaps were similar but detailed investigations revealed significant absorption below the band gap and charge transport that could be described by the Mott variable range hopping (VRH) mechanism over a wide temperature range. These characteristics are manifestations of high intrinsic defect population and crystal disorder despite having achieved single phase pyrite films with Fe:S atomic ratio almost stoichiometric. A careful investigation of charge carrier dynamics in a photoactive nanocube thin film sample by ultrafast transient spectroscopy revealed fast carrier localization and long-lived trap states in the pure pyrite. This is the first time that such a carrier loss mechanism has been elucidated with

experimental evidence in pyrite. Temperature dependent electrical and magnetic behaviors supported the existence of intrinsic localized gap states and vacancies. A non-standard, electrical experiment was carried out in a natural pyrite single crystal sample to assess the surface and bulk resistivities of pyrite which showed a significant difference in them for temperatures less than 120 K. Hence, the surface effect may also have an influence on the charge transport besides defects. It is concluded that the poor photovoltage generated by pyrite solar devices is due to the intrinsic defects in the material rather than to impurities or secondary phases. The effects of the defects on measurable opto-electronic properties are presented and discussed in this thesis. To improve the performance of pyrite devices these defects must be mitigated.

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Abbreviations

EDS	Energy Dispersive X-ray Spectroscopy
RBS	Rutherford Backscattering Spectroscopy
HRTEM	High Resolution Transmission Electron Microscopy
SAED	Selected Area Electron Diffraction
SEM	Scanning Electron Microscopy
HRTEM	High Resolution Transmission Electron Microscopy
XRD	X-ray Diffraction
VRH	Variable Range Hopping
XPS	X-ray Photoelectron Spectroscopy
PLD	Pulsed Laser Deposition
IPCE	Incident Photon to Current Efficiency
EQE	External Quantum Efficiency
SQUID	Superconducting Quantum Interference Device
CE	Counter Electrode
PEDOT	Poly (3, 4-ethylenedioxythiophene)
DSSC	Dye Sensitized Solar Cells

Chapter 1

Introduction

Iron pyrite (FeS_2) is an excellent semiconductor for solar photovoltaic application due its remarkable properties combined with natural abundance. Its band gap (0.95 eV) being close to the solar spectrum maximum, its high optical absorption coefficient (10^5 cm^{-1}) and long minority carrier diffusion length (100-1000 nm) are optimal properties for solar energy harvesting. However, the problem of low photovoltage has plagued the development of pyrite based solar cells. Explanations for this are varied such as bulk and surface defects, stoichiometry deviations, phase impurities, mid gap electronic state formation due to vacancies and symmetry reduction of Fe co-ordination. Incoherent nature of these problems implies that a systematic investigation of the afore-mentioned reasons could enable successful iron pyrite deployment in solar devices. Also, it could allow one to explore new applications related energy devices. The aim of this work is to answer these questions and create a framework of property data for device innovation. Moreover, the basic understanding generated in this work will contribute immensely to the scientific knowledge of photovoltaic systems.

1.1 Hypothesis/Problem Statement

Poor photovoltaic performance of iron pyrite stems from its complex coordination chemistry. Very low open-circuit voltage (V_{oc}) is obtained in devices and that too only by using high quality single crystals. This implies that the problem lies in the material itself rather than on extrinsic factors such as external doping. Pyrite single crystals are universally reported as n-type while films are p-type implying that, in principle, the whole problem condenses to one of defect chemistry and physics of the material, specifically vacancies. However, many factors could contribute to the poor performance of pyrite of which the following important issues will be addressed in this work.

1.1.1 Scientific Issues:

- High quality and phase purity of the films proved by structural characterizations alone does not meet the requirements of high electronic quality and appropriateness necessary for solar cell applications. Then, what characterizations are necessary for a material to assess its suitability for solar cell applications?
- Determine the iron pyrite properties for different product forms such as films, nanostructures and single crystals and establish possible structure-property relationships.
- How the co-existence of unwanted nanoscale phases caused by stoichiometric deviations impact the electronic behavior and whether it introduces significant macroscale property deviation from a normal semiconducting behavior?
- Synthesis of pyrite normally includes a post sulfurization treatment to achieve stoichiometry. Critical evaluation of the necessity of this step is extremely important in the context of pyrite synthesized by different methods.
- Mid gap states and shallow acceptor states are thought to be present in pyrite which could cause rapid thermalization. Determination of the order of carrier relaxation times and the recombination mechanism is crucial.

- Crystal disorder in the material could cause significant variations in the optoelectronic properties. Sub-band gap absorption, nature of the band gap and ubiquitous degenerate semiconducting behavior appear to indicate the presence of disorder in pyrite. However, definite experimental evidence has not been obtained. The related parameters must be measured to assess their impact on transport and optical absorption.

1.1.2 Technical Approach of the Project:

- Investigate scalable synthesis strategies for pyrite thin film fabrication.
- Knowledge of the different charge transport properties in various pyrite product forms such as thin films, nanostructures and single crystals could be used for choosing pyrite for different PV related applications. Identification of such applications and making high performance devices is a technical plus scientific challenge.

1.2 Scope of the Work

Several problems were identified and analyzed in Chapter 2 after a critical literature survey which must be systematically addressed to assess the potential of pyrite in photovoltaic and photonic related applications. Consequently, the scope of this project may be formulated as stated below.

“Synthesis and fabrication of pure pyrite films by various techniques and characterize the structure/defects and relate to optoelectronic properties with emphasis on photovoltaic applications”

1.3 Objectives

Each objective is derived from state of the art of iron pyrite discussed in Chapter 2. Specific objectives of the project are drawn from the general project scope and are proposed below.

- Synthesize high quality single phase pyrite films by spray pyrolysis and conduct structural, optical and electrical characterizations.
- Synthesize nanoparticles by hot injection method and prepare thin films by spin coating.
- Synthesis of iron pyrite thin film by Pulsed Laser Deposition.
- Design an experiment to study bulk and surface conductivities in a high crystallinity and phase pure single crystal.
- Optimize the sulfurization process and study its effects on sprayed films and spin coated nanocubes produced in the project.
- Use femtosecond transient absorption spectroscopy to elucidate the carrier lifetimes and charge recombination mechanisms.
- Evaluation of PV related devices.

1.4 Dissertation Overview

The thesis addresses

Chapter 1 discusses the problem statement and rationale behind the research work. Challenges in the study involved are discussed in a broader context. Specific goals and scope of the thesis are conceptualized.

Chapter 2 provides a critical review of the relevant literature including the latest developments in this field including a historical perspective of the problem. Unresolved issues and gaps in the current state of understanding are identified and highlighted which serve as a backbone for this project.

Chapter 3 discusses the research methodology adopted for this thesis work. Principles and analysis details are discussed for various deposition, characterization and device testing tools deployed in the study. A brief introduction on underlying physics of the research technique used and methods involved are presented.

Chapter 4 describes the synthesis of iron pyrite thin films by spray pyrolysis and subsequent sulfurization. Comprehensive structural, optical and electrical characterization is reported. Their evaluation as counter electrodes in DSSC is also reported here. Reasons for their good performance as counter electrodes are discussed in detail.

Chapter 5 discusses the synthesis of high quality iron pyrite nanocrystals by a solution-based, hot-injection method. A post sulfurization/heat treatment was developed to eliminate insulating ligands. Thin films were prepared by spin coating. Electrical transport and transient absorption spectroscopy results are presented and the possible conduction mechanism and defect structure are deduced. A model is proposed to account for carrier loss processes within the material. Heterojunction solar cells are made and their performance evaluated.

Chapter 6 discusses iron pyrite thin films deposited by pulsed laser deposition using synthetic and natural pyrite single crystal as the target. This is a novel method of making pyrite thin films. Effects of thermal sulfurization and H₂S plasma treatment are investigated. Presence of phase impurity and dynamics of sulfur ingress in the film in both the cases are evaluated.

Chapter 7 deals with the study of natural pyrite single crystal. A special experiment was designed and used to directly probe the surface and bulk electrical resistivities in these crystals. A remarkable divergence in the surface

and bulk resistivity is demonstrated as the temperature is decreased. The results are presented and discussed.

Chapter 8 summarizes the work and attempts to integrate the findings made in other chapters to arrive at some general conclusions relevant for pyrite application in photovoltaic devices. Useful future work is proposed based on the findings of this thesis that might be necessary to make pyrite based devices a reality.

1.5 Findings and Outcomes/Originality

The contributions of this project to the science and engineering of iron pyrite could be listed as below:

- This project has clearly advanced the knowledge of defect physics in pyrite thin films.
- We have demonstrated a possible applications of a pyrite thin film as an efficient counter electrode in DSSC, and spin coated nanocubes in a photodiode and heterojunction solar cells.
- We have identified and correlated the electronic properties of pyrite films fabricated by different methods namely, spray pyrolysis, hot-injection synthesized nanocubes and pulsed laser deposition.
- We have characterized the carrier loss mechanism in pyrite via femtosecond transient absorption spectroscopy for the first time, and developed an electronic state model to explain its experimental behavior. This elucidates the poor photovoltage observed by all researchers previously.
- We have demonstrated the possibility of production of pure pyrite thin films by pulsed laser deposition for the first time.

- We have critically tested literature that phase and elemental impurities are the causes for the poor photovoltage generation in pyrite PV devices. It is shown that even pure phase pyrite exhibits poor photovoltage and this is attributed to intrinsic crystal defects in the material, particularly vacancies.
- We have confirmed that the surface and bulk resistivity values of a pyrite single crystal diverge significantly at temperature below 120 K as some recent reports.

Chapter 2

Literature Review

This chapter is a critical review of relevant literature on iron pyrite. A Historical perspective is presented in the context of photovoltaic application of iron pyrite. Iron pyrite solar cells have been difficult to realize due to low photovoltage. The problem of low photovoltage is commonly attributed to bulk and surface defects, such as vacancies and phase impurities and surface inversion layer. Several attempts have been made to prepare high quality films with fewer defects. This literature survey provides a detailed summary of the properties obtained from different pyrite films, crystals and nanostructures. Major scientific challenges that still remain to be addressed are the impact of intrinsic defects on optoelectronic properties of pyrite. Material synthesis related issues and devices have been highlighted and discussed from which the scope and objective of this work are drawn.

2.1 Global Energy Scenario

Energy is the ultimate solution to many problems prevailing in our society. It can be readily stated that the quest for energy is one of the biggest challenges of the modern era. Global energy demand is continuously increasing and energy in the form of electricity is a major driving force of the economy and human development.¹ Currently, the worldwide electricity usage is estimated to be around 16 TW and is expected to double (~ 30 TW) by year 2050.² Conventional sources of energy such as oil, natural gas and coal are restrained as there are limited reserves worldwide. Such conventional energy sources are still fulfilling most of the energy requirements of the world.³ Although, these sources appear affordable at present, it is certainly not going to be the same in the long run. On the other hand, fossil fuel based energy sources are key contributors to carbon emissions, posing the risk of global climate change⁴. Also, dissolution of CO_2 in water makes it more acidic and endangers marine life. This is commonly termed as the effect of “Global warming” and has a debilitating impact on our climate.⁵ Thus we see that the problem of energy and environmental sustainability are closely related. The challenge is to harness energy in a sustainable manner. Thus, the requirement of a disruptive energy technology is essential. *“The stone age did not end because we ran out of stone”*.⁶

Sun is a nearly inexhaustible source of energy. It provides energy in the form of electromagnetic radiation that falls daily on the earth. Energy illuminating the earth every hour is equivalent to 1-year electricity consumption worldwide. Figure 2.1 depicts the enormous potential of solar energy in comparison to other energy sources. The big yellow circle in the figure occupies a huge area depicting amount of energy that could be harnessed from the sun.

Figure 2.1 The potential of solar energy in comparison to other renewable and non-renewable energy sources. Solar energy (big yellow sphere) overshadows all other energy alternatives. (Source – R. Perez & M. Perez, A Fundamental Look at Energy Reserves for the Planet)

Converting solar energy to electricity efficiently would enable gigawatt scale energy production without emitting deleterious gases and polluting the atmosphere. The major obstacle to widespread adoption of solar energy is the scalability and cost concerns.

Inorganic semiconducting materials are most useful in this context as these materials can be readily processed on a large scale to make thin film photovoltaic devices.⁷ Silicon dominates the solar energy market by taking 90 % of the market share while the thin film solar cells using materials such as CdTe, CIGS etc. occupy the balance. Relatively thicker films ($\sim 300 \mu\text{m}$) of Si are required to absorb most of the photons due to its lower optical absorption. Higher absorption materials would permit thin film cells to be used reducing the requirement for the high quality material. Commercial thin film solar cell technology is currently based mostly on CdTe, CIGS, while new materials are constantly being explored in research laboratories.⁸ Solar energy spectrum dictates that a band gap of

around 1.5 eV would be ideal for optimum absorption of photons in the spectrum.⁹

Requirements for a good solar absorber are –

- high optical absorption coefficient.
- high quantum efficiency.
- high excited charge carrier collection efficiency.
- long diffusion length.
- low recombination velocity.

Si, an indirect band semiconductor with a gap of 1.1 eV, offers conversion efficiencies of around 25 %. However, the processing cost to produce the high quality and purity required for solar cells is posing a problem for greater market penetration. To address the cost issue, thin films of high optical absorption, alternative materials such as GaAs,¹⁰ CdTe,¹¹ Cu₂S,¹² Cu₂O,¹³ InP,¹⁴ Zn₃P₂,¹⁵ CISE,¹⁶ CIGS,¹⁷ CZTS¹⁸ and FeS₂ have been investigated. Among these materials, thin films of GaAs and, InP gave promising efficiency values but their material cost and toxicity concerns have to be addressed before their adoption as commercial PV. CdTe, on the other hand, is a commercially viable PV material and is only behind Si in performance, but its commercial applicability is yet to be tested in terms of cost and market potential. While other materials evaluation is still in the nascent stage and their fundamental physics need to be understood. Raw materials availability and scalable processing are two major aspects for commercialization and sustainable solution. Binary systems (CdTe, GaAs etc.), although, promising but limited by materials availability while ternary and quaternary systems (CISE, CIGS etc.) are complex due to the need for controlled, multi-component processing. FeS₂ being a simple binary compound, is a potential candidate and gained considerable interest among the PV community due its abundance and remarkable optoelectronic properties.

2.2 A Brief Historical Review of Pyrite

Iron pyrite (FeS_2) is among the primitive materials that was analyzed by Lawrence Bragg in his first X-ray crystallographic studies in 1913.¹⁹ The word “pyrite” is of Greek origin which means “fire”, a term associated with the stones that generate fire. The pale yellow color and metal-like lustrous appearance of the natural pyrite crystals closely resembles gold. It is often referred as “fool’s gold” and became the reason for the embarrassment of the miners of the “California gold rush”, who mistakenly attributed the pyrite to gold. Apart from these historical facts, pyrite gained massive interest in the field of solar photovoltaics (PV). Its excellent semiconducting properties in conjunction with abundance, makes pyrite an ideal candidate for solar absorber material.²⁰ The research on pyrite based solar cell started in 1980s led by Prof. Helmut Tributsch at Hahn-Meitner-Institut, Germany.²¹ Despite their focused research effort, its solar to electricity conversion efficiency remained too low. However, the high quantum efficiency displayed by pyrite crystals motivated the researchers to synthesize high purity material to increase the solar cell efficiency. The improvement in efficiency was hampered mainly by the limited photovoltage generated by the cells.²² It was concluded that the stoichiometry variations inherent in the crystals cause intrinsic defects and lead to poor performance.²³ Eliminating these defects proved to be extremely challenging and their correlation with optoelectronic properties of pyrite remained a mystery.

2.3 Basic Material Properties

Pyrite belongs to the AB_2 type crystal structure family where the cation A is generally a transition metal (Fe, Co, Mn etc.) and B can be an element from group V pnictides (P, As, Sb) or chalcogenides (S, Se, Te). Iron pyrite has a cubic NaCl type crystal structure where Fe^{2+} ions occupy Na sites while sulfur dimers (S_2^{2-}) occupy Cl^- ion positions. Iron disulfide belongs to space group $\text{Pa}\bar{3}$. Fe atoms are

positioned in a face-centered cubic (FCC) sublattice, in which sulfur dimers are oriented along $\langle 111 \rangle$ direction. Each Fe atom is octahedrally coordinated with six sulfur atoms and a sulfur atom is tetrahedrally coordinated with three Fe atoms and one sulfur atom. Local point group symmetry of Fe atom is O_h (octahedral) in the bulk while at the surface, it reduces to trigonally distorted octahedral (C_{4v}) due to the reduced sulfur coordination.²² The local sulfur atom symmetry is tetrahedral (C_{3v}). FeS_2 has a polymorphic phase called “marcasite” which has an orthorhombic crystal structure. Pyrite and marcasite have similar energies of formation and, hence it is often challenging to obtain pure phase pyrite in films.²⁴ In the next section, we will discuss thermodynamic aspects of the Fe-S system.

2.3.1 Thermodynamics: Phase diagram and instabilities

The Fe-S phase diagram is shown in Fig. 2.2. It is evident that pyrite phase field is confined within a narrow region of composition indicating it to be a line-phase that is almost stoichiometric, as indicated by red box in Figure 2.2. Slight variations in the growth conditions and composition would result in other phases such as FeS (troilite), $Fe_{1-x}S$ (pyrrhotite) and Fe_3S_4 (greigite) etc. to appear.²⁵

Figure 2.2 Phase diagram of Fe-S system²²

Pyrite decomposes at 743° C to pyrrhotite and subsequently to FeS as given in Equation 2.1

The fact that this decomposition happens much below the melting temperature of pyrite, makes it difficult to grow pyrite crystals by classical crystal growth techniques such as Bridgman growth method. Moreover, the difference in the binding energy of sulfur at the surface and bulk leads to surface decomposition at elevated temperatures.²⁶ Hence, a consideration of phases encountered during pyrite growth or synthesis is of extreme importance. Normally under diffusion limited growth conditions, FeS₂ growth is facilitated by intermediated sulfur deficient phases such as FeS. Sulfur diffusion is quite sluggish in such phases.²⁷ Therefore, high sulfur vapor pressures are required for complete phase conversion.²⁸

2.3.2 Electronic Structure

Electronic structure of pyrite results from splitting of hybridized Fe d orbitals and S p orbitals which is explained by the Ligand Field Theory (LFT). When the positively charge Fe ion bonds with negatively charged S ligands in its neighborhood, the Fe 3d states split as a result of ligand field and give rise to energy bands. These bands are formed due to the orbital overlap of Fe 3d states with hybridized sulfur 3p and 3s states. Depending on the overlap, the electrons are localized (in d states) or delocalized (within energy band formed due to overlap).²⁹ Figure 2.3 shows the distribution of density of states of pyrite. Fe d states split to triply degenerate t_{2g} and doubly degenerate e_g orbitals under the approaching octahedral field of sulfur ligands. e_g orbital forms the conduction band and lies higher in energy due to antibonding nature and hence the electrons in e_g states experience repulsion. Low lying t_{2g} bonding states form the valence band. Distribution of electrons in these states is such that the configuration maximizes the crystal field stabilization energy Δ . As a consequence, pairing energy is favored, leading to completely filled t_{2g} states with paired electrons (d^6). This low spin configuration is responsible for the diamagnetic nature of pyrite.^{30,31}

Energy difference between e_g and t_{2g} states is defined as energy band gap of iron pyrite. This corresponds to widely accepted band gap value of 0.95 eV – 1.10 eV. Valence band character is mainly due to sulfur 3p convoluted with narrow localized Fe 3d t_{2g} state while conduction band e_g states comprised mainly of mixed 3d Fe orbitals with hybridized sulfur $3p\sigma^*$ orbital. However, theoretical studies has shown that the conduction band minima is mainly dominated by sulfur $3p\sigma^*$ hybridized orbitals.³²

Figure 2.3 (a) Schematic of the distribution of the density of states in iron pyrite formed due to Fe 3d and S 3p orbitals, (b) Band structure of bulk iron pyrite.²²

2.4 Defects in Pyrite

Defects in the semiconductor play a crucial role in PV performance. Some defects could be advantageous for device performance, and are deliberately created by doping the material in a controlled manner. While other defects could be detrimental to the device performance making it acts as a “leaky bucket”. The complex electrical behavior of pyrite points to the presence of a complex defect structure.³³ The narrow window of thermodynamic stability of pyrite gives plenty of opportunities for off-stoichiometric defects to form. Extreme stoichiometric variations may result in a coexistence of alternative, unwanted phases such as orthorhombic FeS_2 (marcasite), Fe_{1-x}S (pyrrhotite), Fe_3S_4 (greigite), FeS_{1-x} (mackinavite) and FeS (troilite) etc.³⁴ All these unwanted phases have low band gaps and thus could introduce mid-gap states in the pyrite.

Studies on natural, as well as synthetic, high quality pyrite single crystals have shown them to have n-type conductivities with high mobilities. This is in contrast to observations in pyrite thin films, which ubiquitously show p-type conductivity

with low carrier mobilities.³⁵ Moreover, the low photovoltage (V_{oc}) obtained using both pure pyrite crystals and thin films points to the presence of intrinsic defect structures that are quite different. Intrinsic defects commonly result from S vacancies (V_s) and Fe vacancies (V_{Fe}) for n-type and p-type doping respectively. However a complete understanding of the defect structure is still lacking. Hopfner and Ellmer claim that pyrite is a strictly stoichiometric compound and hence large deviations from stoichiometry is not anticipated.³⁶ This argument is based on high vacancy formation energies of V_s and V_{Fe} . This claim is contrary to the experimentally observed off stoichiometric compositions as high as 7 % (FeS_{2-x}).³⁷ First principle density functional theory (DFT) calculations show high Fe and S vacancy formation energies in the bulk, ruling out the possibility high concentration of bulk defects. Under sulfur rich conditions, V_{Fe} formation energy (1.82 eV) is low while in iron rich conditions, V_s formation energy (2.42 eV) is low.³⁸ Nevertheless, these formation energies are still thermodynamically high enough to cause vacancies that are experimentally observed. This is controversial and requires more theoretical attention. Another important consideration is the presence of phase impurities. Sulfur vacancies, which are commonly interpreted as point defects, could be readily accommodated locally by the formation of low band gap Fe-S phases.^{39,40} Owing to their close thermodynamic enthalpies, FeS_2 could readily decompose into sulfur deficient phases such as FeS_{1+x} ($0 \leq x \leq 1$). Thus, the final outcome could be pyrite coexisting with other phases.⁴¹ This agrees well with the commonly observed degenerate semiconductor behavior with significant sub-band optical absorption which is attributed to the poor solar photovoltaic performance of pure pyrite, both in single crystal and thin film forms.^{42,43} However, this explanation is too speculative with insufficient scientific evidence and thus requires further experimental verification for confirmation. Moreover, the impact of marcasite impurity on solar cell performance and its electrical properties are still not fully understood.

Figure 2.4 Density of states of pyrite in octahedral co-ordination, valence band maxima is formed from t_{2g} state and conduction band minima is formed from e_g state. Reduced co-ordination of Fe due to sulfur vacancies lead to splitting energy states creating levels within the band gap.²²

Ligand field theory (LFT) or molecular orbital (MO) theory provides qualitative explanation for the energy bands and defect states due to the change in Fe-S co-ordination. For example, Jaegermann and Birkholz analyzed the sulfur deficiency in context of reduced sulfur co-ordination and its effect on the energy bands. Figure 2.4 shows the energy band diagram after reduced sulfur co-ordination from FeS₆ to FeS₅.³⁷

2.4.1 Surface Problem

Although the intrinsic bulk defects are difficult to form due their high formation energy, surface of pyrite is highly prone to defects. Formation of sulfur deficient phases and conducting FeS surface layers is also a plausible explanation for the poor photovoltaic performance of pyrite. High density of surface defects can potentially pin the surface fermi level and induce strong band bending near the

surface creating a hole rich inversion layer. Bronold et al. argued that even a simple symmetry reduction at the surface due to the reduction of Fe co-ordination from O_h to C_{4v} could form defects states and hence an inversion layer at the surface.⁴⁴

Figure 2.5 (a) Energy band bending scheme in pyrite single crystal proposed on the basis of various measurements,⁴⁵ (b) Projected DOS in a thin pyrite slab, black lines depicting carrier excitation in the bulk and quick relaxation into the surface states.⁴³

Jin et al. showed that such defect states energetically lie within the band gap of iron pyrite. Charge neutrality requires charge transfer from the bulk to the surface. This leads to the upward band bending at the surface and inversion of the majority carrier type (from n-type in the bulk to p-type at the surface) as shown in Figure 2.5 (a). Thus, deep ionized donor states from the bulk severely affect the surface potential causing low photovoltage.⁴⁵ On contrary, Law et al. explains the problem of low photovoltage and Fermi level pinning due to surface defects alone.⁴⁶ The study on surface inversion was reported for single crystal pyrite. Could this be extended to polycrystalline pyrite thin films? We believe it could be but cautiously. The carrier dynamics and charge transport through these defect states also need to be examined. Additionally, this also changes the electronic configuration of pyrite from low spin to high spin configuration with high electrical conductivity that is sometimes observed in pyrite samples indicating a metallic state at the surface. Accompanying surface band gap reduction is also attributed to the metallic behavior providing conducting pathways. Ceder et al. argued that low intensity S p-bands convoluted with conduction band, provide

finite density of states that form band tails. These band tails could be connected to the surface states that typically form within the forbidden band gap. Thus, excited charge carriers in the bulk quickly thermalize through the surface states before getting collected as shown in Figure 2.5 (b).⁴³

2.5 Previous Research on Pyrite

Previous research activities on iron pyrite have attempted to address two major issues:

- (1) Synthesis of high quality material,
- (2) Poor solar cell performance.

Although, pure pyrite is among the common materials to be studied by crystallographers due to its simple cubic structure, synthesis of high quality crystals and films have been challenging. Phase impurity and stoichiometry control appear to be the most difficult challenges during the synthesis. Due to lack of control on phase impurity and stoichiometry, the reported electronic properties of iron pyrite varied significantly and remained unpredictable. A careful analysis of the literature shows variability in intrinsic material properties from different synthesis techniques. Table 2.1 lists pyrite films and crystals made by different methods and their respective electronic properties.

Table 2.1 Iron pyrite synthesized by various techniques and corresponding properties

Technique	Product	Properties	Highlights
MOCVD ⁴⁷ (2000)	FeS _{1.985-2.076}	E _g = 0.9-1.1 eV p-type $\rho = 0.5\text{-}1\ \Omega\text{-cm}$	H ₂ required
Sulfurization of Fe thin films ⁴⁰ (2013)	(i) FeS _{1.88+-0.10} (ii) FeS ₂	n- type, $n = 10^{20-21}\text{ cm}^{-3}$ $\rho = 0.5\ \Omega\text{-cm}$, $\mu = 0.1\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ E _g = 1 eV, p-type, $\rho = 0.1\ \Omega\text{-cm}$,	Crossover from n-p type Stoichiometry not clearly stated, Fe (n-type) – Fe _{1-x} S – FeS ₂ (p-type)
Sputtering ⁴⁸ (1992)	FeS ₂	E _g = 0.6 eV (Indirect), 1.5 (direct), p-type, $p = 5 \times 10^{18}\text{ cm}^{-3}$, $\rho = 0.2\ \Omega\text{-cm}$, $\mu = 5\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$	Sulfur assisted magnetron sputtering
Electrodeposition ⁴⁹ (2005)	FeS ₂ *	E _g = 1.3 eV, p-type, $p = 10^{14}\text{ cm}^{-3}$, $\mu = 200\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$	Sulfurization at 500° C
Chemical bath deposition (CBD) ⁵⁰ (2013)	FeS ₂ *	E _g = 0.85 eV, p-type, $p = 3 \times 10^{17}\text{ cm}^{-3}$, $\rho = 0.5\ \Omega\text{-cm}$, $\mu = 14\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$	Phase impurity, sulfurization at 400° C (Fe-O-S system)

CVD ^{34,51,52} (2012, 2003, 2015)	(i)	FeS _{1.98}	$E_g = 1$ eV, n-type, $n = 5.5 \times 10^{17} \text{ cm}^{-3}$, $\rho = 0.97 \Omega\text{-cm}$, $\mu = 280 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$	Single crystal thin films on Si substrate FeCl ₃ +
	(ii)	FeS _{2.00 ± 0.06}	$E_g = 0.97$ eV, p-type, $p = 10^{18} - 10^{20} \text{ cm}^{-3}$, $\rho = 1 \Omega\text{-cm}$, $\mu = 1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$	CH ₃ CSNH ₂ Fe(acac) ₃ + TBDS
	(iii)	FeS ₂ *	$E_g = 0.76$ eV (direct), n-type, $n = 2 \times 10^{21} \text{ cm}^{-3}$, $\rho = 1 \Omega\text{-cm}$	chemistry – atm + Sulfurization Direct CVD
Chemical Ink ³⁵ (2013)		FeS ₂	$E_g = 0.87$ eV, p-type, $\rho = 1.9 \Omega\text{-cm}$, $\mu = < 1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$	Air annealing + H ₂ S annealing + S annealing
Chemical vapor transport ^{45,53} (2014, 1992)	(i)	FeS ₂ Single crystal	$E_g = 0.81$ eV (direct), n-type, $n = 1 \times 10^{15} \text{ cm}^{-3}$, $\rho = 3 \Omega\text{-cm}$ $E_g = 0.95$ eV	Crossover to hopping transport at low temperature
	(ii)	FeS ₂ single crystal	(Indirect), n-type, $n = 10^{16} - 10^{17} \text{ cm}^{-3}$, $\rho = 0.1 \Omega\text{-cm}$, $\mu = 185 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$	and Hall coefficient change Small Hall voltage, High sulfur

				pressure
				annealed
				crystals p-
				type
Flux growth ^{46,54} (2014, 1993)	(i)	FeS ₂	$E_g = 0.94 \text{ eV}$ (Indirect), n-type, $n = 5 \times 10^{15} \text{ cm}^{-3}$, $\rho = 1\text{-}10 \text{ }\Omega\text{-cm}$, μ $= 245 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ $E_g = -$, n-type, $n =$ $3 \times 10^{16} \text{ cm}^{-3}$, $R \sim$	p-type inversion layer observed at the surface
	(ii)	FeS ₂	$3 \text{ }\Omega\text{-cm}$, $\mu = 100$ $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$	
				Mobility limited by ionized impurity scattering

It can be noted that crystals are mostly reported to be n-type with low carrier concentration and high mobilities while films are mostly p-type (with few exception) with high carrier concentration and low mobilities. Therefore, a reasonable explanation would be to assume that the p-type conductivity in films is caused by the dominance of the surface. The situation could be extrapolated to nanostructures which have large specific surface areas where dominance of p-type conductivity could be expected.⁵⁵⁻⁵⁷ Nanostructures provide the flexibility of high quality material and better stoichiometric control through surface treatments and post annealing processes. Figure 2.6 shows the mobility vs carrier concentration plot for various pyrite forms such as crystals, thin films and nanostructures. Although a clear distinction could be made between the different

forms *viz* crystals, thin films and nanostructures, there has been little explanation for n-type and p-type difference and spread in the values of mobility and carrier concentration based on structure-electronic property relationships. Recent findings on iron pyrite single crystals confirm the existence of p-type inversion layer at the surface with n-type bulk material.⁴⁶

Figure 2.6 Data points taken from the literature for Hall mobility vs carrier concentration for various pyrite crystals, thin films and nanostructures. Crystals with high mobilities showing n-type while films and nanostructured pyrite have low mobilities and show p-type conductivity.

2.6 Iron Pyrite Devices

Highest efficiency of solar performance reported in iron pyrite to date is in a photoelectrochemical liquid junction solar cell. Photoconversion efficiency of 2.8 % was reported with J_{sc} of 42 mA/cm², FF 0.5 and V_{oc} of 187 mV under 100 mW/cm² illumination. (Cited as ref. 22, the original report appeared in “Proceedings of the 1st World Renewable Energy Congress, 23. - 28 Sept. 1990, Reading, UK, Vol. 1: 458-464”). Note that the efficiency was reported for a liquid junction of pyrite single crystal in iodine/iodide redox electrolyte. In addition, remarkably high quantum efficiency was also achieved (> 90 %). This efficiency still remains unsurpassed even after 30 years of this original report, shown in Figure 2.7 (a). In the above sections, I discussed the properties of pyrite and it becomes apparent that the attained conversion efficiency is not even half of the

value that could be potentially achieved in pyrite containing solar cells. The poor efficiency is frequently attributed to low photovoltage output which is, in turn, relates to the defect physics discussed in the above sections of this chapter. However, a clear mechanism with convincing experimental and theoretical evidence is still not available. A recent attempt to make PEC from a high quality CVT grown pyrite single crystals has shown similar low performance with photovoltage of around 100 mV.⁴⁵

Figure 2.7 Current-voltage characteristics of photoelectrochemical solar cell using (a) n-FeS₂ synthetic crystal with iodine/iodide redox electrolyte,²² (b) (100) faceted n-type FeS₂ single crystal using aqueous and non-aqueous electrolytes.⁴⁵

Various aqueous and organic electrolyte redox couples were studied but the photovoltage remained low. A key step towards realizing pyrite devices appears to be to understand the role of defects in influencing the carrier transport properties and recombination mechanism. As previously discussed, carrier densities significantly differ for pyrite made by different synthesis approaches. For solar cell application, a low carrier density pyrite is suitable. This could be an advantage to deploy pyrite films for other optoelectronic and electrochemical application also such as a photodiode, catalyst and battery. Low cost and scalable synthesis of pyrite for such application is highly desirable.

A photodiode fabricated from pyrite exhibited good photoresponse in various architectures. Figure 2.8 shows the performance of different pyrite films in various configurations.

Figure 2.8 (a) Photodiode made from FeS₂ nanocrystals⁵⁸, (b) Pyrite nanowires photodetector showing photoresponse.⁵⁹

2.7 Research Status Summary and Discrepancies in the Literature and this Project in Perspective

Significant attention and effort have been focused on pyrite for photon excitable applications. Synthetic routes have been developed to address the problem of stoichiometry deviations and phase purity. However, there are still major roadblocks to enable pyrite use in photovoltaic application. The status of current research developments can be listed as below –

- The low photovoltage obtained from pyrite solar cells is the main issue. Many explanations have been offered but they are inconclusive. Hence, the reason is still unknown. This project intends to provide a deep insight into this problem.
- There is a significant spread in the carrier concentration and mobility values reported in the literature for different pyrite product forms namely, crystals, films and nanostructures, which makes it necessary to systematically characterize their structure and properties. This will be undertaken in this work. Pyrite films, nanostructures and crystals will be produced with different carrier concentrations and mobilities, and will be correlated to the electrical and optical properties.

- Intrinsic defects are a possible cause for the poor performance of pyrite solar cells. In this project, pyrite films will be made by different techniques such as spray pyrolysis, spin-coating and pulsed laser deposition to obtain films with different defect and population and their optical and electrical properties will be measured and compared.
- Post sulfurization treatment is used to ensure the formation of pure pyrite phase and achieve better crystallinity. This treatment is considered an important step to obtain high quality films. However, the sulfurization treatments reported in the literature are not rationalized. In this work, sulfurization conditions are will be rationalized and a standard treatment will be proposed.
- Different bulk and surface conductivities caused by a surface inversion layer in pyrite crystal is discussed in the literature. Novel, sensitive experimental techniques are necessary to investigate the difference between bulk and surface conductivities. In this work, a new experimental procedure is designed based on proposals in the literature, to measure the resistivity in the bulk and surface of a single crystal.
- Electrical transport studies report hopping transport at low temperatures. However, there are inconsistencies in these reports with respect to the mechanism of transport. Explanations vary from Mott type, to Efros-Shklovskii, to intergranular hopping. Electrical transport in pyrite films will be studied on different types of films to clarify the mechanisms.
- Band tailing in pyrite is frequently hypothesized in the literature as a major loss channel for carrier relaxation. Understanding the carrier relaxation mechanism and quantification of carrier lifetimes are clearly lacking in the state-of-the-art. This project will look into this issue and try to quantify the carrier lifetimes and elucidate the carrier loss mechanism in pyrite.

- Synthesis of pyrite in the literature is limited to growth techniques such as CVD, sputtering, colloidal inks. The high vacuum based depositions such as MBE, ALD and PLD has not been explored. The high vacuum techniques are frequently used to get extremely high quality films. In this work, PLD will be employed for the first time to produce high quality, single phase pyrite films.
- Different PV related devices are proposed for pyrite applications in the literature for different purposes. This highlights the potential of pyrite to be used in different devices. Accordingly, different pyrite based devices will be fabricated and assessed in this project.

2.8 Scope

Following the comprehensive literature survey and analysis, several problems were identified which must be systematically addressed to assess the potential of pyrite in photovoltaic and photonic related applications. Consequently, the scope of this project can be formulated as stated below.

“Synthesis and fabrication of pure pyrite films by various techniques and characterize the structure/defects and relate to optoelectronic properties with emphasis on photovoltaic applications”

2.9 Objectives

To facilitate the project planning and implementation several specific objectives are formulated within the above scope. These are listed below and were used to give guidance throughout this project period –

- **Synthesize high quality single phase pyrite films by spray pyrolysis and conduct structural, optical and electrical characterizations.**
 - Spray pyrolysis is a commercial process used to fabricate many films, including pyrite. Control of stoichiometry was found to be challenging by previous works.
- **Synthesize nanoparticles by hot injection method and prepare thin films by spin coating.**
 - Spin coating is an alternative way of making films particularly in microelectronics industry while hot injection method could produce well controlled nano particles by solution-based method.
- **Synthesis of Iron pyrite thin film by Pulsed Laser Deposition.**
 - PLD is a good way to prepare high quality experimental films in the laboratory. Since, this method has not been employed by any previous workers for pyrite films, the results obtained here could be interesting for comparison with other films.
- **Design an experiment to study the bulk and surface conductivities in a pyrite single crystal.**
 - This is a novel element in the project to verify the presence of the surface inversion and its effects.
- **Optimize the sulfurization treatment and study its effects on sprayed films produced in the project.**
 - This is to standardize the sulfurization treatment.
- **Use femtosecond transient absorption spectroscopy to elucidate the carrier lifetimes and charge recombination mechanisms.**
 - This is an advanced technique that could throw a lot of light on the photo physics in materials. This has not employed on pyrite previously. This will be the first attempt at understanding the photo physics of pyrite through this technique. This will be done on the most suitable films produced in the project.

- **Evaluation of PV related devices.**
 - Fabricate suitable devices to evaluate the performance of pyrite films in the intended applications.

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Chapter 3

Experimental Methodology

This chapter deals with the principles of the experimental methodology adopted to prepare pyrite thin films and characterize them. Synthesis details and film deposition mechanisms are discussed. In this study, spray pyrolysis thin film deposition technique, hot-injection method for nanoparticle synthesis and pulsed laser deposition of thin films will be discussed. Various structural, optical, electrical and solar device related characterization tools and data analysis techniques adopted in this thesis work are presented. Complete description of the experimental set up and underlying principles of the respective characterization method is described.

3.1. Material Synthesis and Thin Film Preparation

Iron pyrite thin films were prepared by three different methods, namely spray pyrolysis, films made from hot-injection synthesized nanocubes and pulsed laser deposition. The above mentioned deposition methods produce film of different defect concentrations and morphology which may have an impact on electrical properties of pyrite. Spray pyrolysis method is relatively simple and does not require vacuum chamber or any gas ambient for deposition.¹ Large scale deposition of pyrite films is achievable by spray pyrolysis. However, there is a less control on composition in the process. On the other hand, hot-injection method provides good crystalline quality, size and shape control and the chemical composition of material.² Pulsed laser deposition of iron pyrite thin films is a novel element in this project. PLD is method to prepare thin films with precise control on chemical composition.³ Since the deposition is done in the vacuum with a target of known chemical composition, better control on the film chemical composition is obtained over the other two methods.

Sulfurization process (heat treatment under sulfur ambient) was done after the film deposition to obtain good crystallinity and phase purity of the films prepared by spray pyrolysis and PLD process. While in the case of nanocubes, sulfurization process was done to prevent sulfur loss from the nanocubes during the heat treatment. Thus, three types of films produced in the project possess different defect densities and morphology. This forms the basis of the comparison of optoelectronic properties of different films to get detail insights on the defect mechanism of iron pyrite.

3.1.1 Spray Pyrolysis for Thin Film Deposition

Spray pyrolysis is a simple method to prepare thin films that involves inexpensive precursors and minimal equipment cost with rapid scalable processing. Technique has been commercially applied to obtain transparent conducting glasses (Sono-tek company). While in research, many semiconducting materials such as ZnO,⁴ SnS,⁵ CdS,⁶ CIGS,⁷ CZTS⁸ has been prepared by spray pyrolysis for various device application. For this project work, spray pyrolysis method is adopted to prepare thin films of pyrite. Availability of the appropriate aqueous precursors of desired chemical activity makes it possible to prepare polycrystalline thin films easily.

There are number of parameters that affect the growth rates and film quality. Critical components of the process include atomizer, appropriate precursor, hot plate with uniform temperature heating zone. Film is formed at the hot surface by the reaction of precursor at suitable temperature. The basic steps of the process are written below

- (1) Metal salts and chalcogen precursor is chosen. Decomposition temperature and right oxidation states are important for the reaction to happen. These are the two key parameters to be considered while choosing the precursors. For iron pyrite synthesis, I have used $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (iron chloride hexahydrate) as iron precursor and $(\text{NH}_2)_2\text{CS}$ (thiourea) as sulfur precursor.
- (2) Solvent is required to dissolve precursors to be sprayed. Precursor solubility has to be good in the chosen solvent. Water is used as a solvent for iron pyrite synthesis studied in this thesis work.
- (3) Spray of the precursor is formed by atomizer. Air blast is commonly used to produce precursor mist. Solution is air blasted by the pressurized flow of the

gas. Nitrogen gas is fed in a spray gun connected to the solution is used in this work.

- (4) The most important parameter to initiate the reaction at the surface is the temperature of the substrate placed on the hot plate. Substrate temperature has to be high enough to cause pyrolytic decomposition to occur and reaction to initiate. Temperature also plays important role in spreading the precursor droplets evenly and merge to form a continuous film. The mechanism of the film formation is discussed in detail in the subsequent section.

Schematic of the process described above is shown on figure 3.1

Figure 3.1 Schematic of the spray pyrolysis set up.

3.1.1 (a) Chemistry of Spray Pyrolysis Deposition

Reactive species of Fe and S precursors in appropriate amount in an aqueous solution was sprayed on a hot surface to form a Fe-S complex. Nitrogen gas was used as a carrier gas to transport precursor solution to the hot surface with controlled flow rate and coverage. At hot surface, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and thiourea decompose thermally and react according to the following chemical reaction⁹ –

Thermal hydrolysis breakdown leads to decomposition of FeCl_3 and thiourea. Thiourea reduces the Fe (III) species in FeCl_3 to Fe (II) providing the necessary Fe initial reactant. Sulfur reactants are provided in the form of polysulfides and H_2S by decomposition of thiourea. So thiourea serves dual purpose, one is providing sulfur reactant flux and reduction of Fe (III) to Fe (II). The process need not be done in the vacuum. In fact, oxygen present in the ambient assists in the formation of CO_2 to remove the unwanted carbon during the reaction. Previous studies report the presence of pinholes in the film which are attributed to the gaseous CO_2 within the film.⁹ Ambient spraying provides enough oxygen to react with carbon.

3.1.1 (b) Film Formation Mechanism

Number of parameters such as substrate temperature, gas flow rate, droplet size, substrate to spray nozzle distance and solution concentration etc. affect the film morphology. Transportation of spray droplets to the surface and reaction at the surface determines the morphology. Droplets decompose near the hot surface and precipitates as product while solvent evaporates and gaseous byproducts evolve at the surface. Larger spray droplets result in a large particle size due to incomplete decomposition of the precursor. On contrary, very small particle size evaporates too fast forming products near the surface and precipitates. This leads to non-adherent films. Optimal combination of droplet size and temperature yields continuous adherent films at the surface. In the present case, substrate temperature is held at around 350°C and spray nozzle was moved mechanically in X-Y direction to spray uniformly. It is important to note here movement of the spray gun should be such that it allows the surface to remain at the high temperature. Liquid droplet falling on the surface cools the substrate, so laterally moving the spray gun avoids that problem. One of the highlight of spray pyrolyzed thin films is the roughness. Spray deposition can be thought of as particle accumulation and coalescence process, normally leading to rougher film

morphology. Especially at higher temperatures, film is more rough and porous which is advantageous for certain applications such as high surface area catalysis.

Thus, spray pyrolysis is a robust way of thin film preparation. Tuning the parameters can give desirable films with different compositions just by changing the molar ratios of the precursor solution. No constraints on substrate type makes the process compatible with different characterization and device platform. Good iron and sulfur precursor source availability, compatibility to aqueous solvent, suitable decomposition temperatures and appropriate oxidation states makes it extremely favorable to deposit iron pyrite thin films. Spray pyrolysis process is conceptually similar to do heterogeneous chemical vapor deposition growth. However, the later involves the use of complex and sometimes toxic gaseous precursors (for example Iron pentacarbonyl $\text{Fe}(\text{CO})_5$, thioacetamide $\text{C}_2\text{H}_5\text{NS}$, tert-butyl disulfide etc.) under inert controlled ambient. Spray deposition certainly gives a fast, easy and scalable alternative to obtain thin films with multifold reduction in the complexity. Despite so many advantages, there are inherent challenges and limitations of the technique. Post annealing treatment is generally required after spray deposition to provide enough partial pressure of the reactant and consequently achieve high crystallinity and phase. This thesis covers the post annealing analysis on the film pyrite films made by spray pyrolysis.

3.1.2 Hot-injection Method to Prepare Nanostructures

Colloidal nanocrystals have received significant amount of interest and attention since last decade. The precise control of size, shape and quality control along with solution based simple “in-flask” reaction offers a whole new area of exciting devices and physics. This enables deeper understanding of the material-structure-composition-size relationships. Small nanocrystals are the tiny components of a complete system of nanoparticles either self-assembled or prepared by simple

coating techniques.² Hot-injection method is a widely adopted technique for nanoparticle preparation. It utilizes one of the fundamental laws of melting point change as dimensionality or size is reduced to nanoscale regime. Small nanoparticles possess high surface-to-volume ratios, resulting in a significant surface energy and low melting points. Thus, a wide variety of materials can be made which would otherwise be difficult to synthesize in gas phase (e.g. CVD). In the context of iron pyrite, nanoparticle synthesis has revived the interest in the field due to better control on size, phase purity and crystallinity etc. aiming to answer fundamental bottlenecks of pyrite and offer solutions for better device performance.¹⁰

3.1.2 (a) Basics and Growth Mechanism

The major components of the reaction consist of a precursor, surfactants (ligands) and solvent. Precursor is generally a compound consists of reactive species pertaining to the formation of the product. Respective precursors dispersed in the solvent, gets thermally dissociated into chemically active molecular species often called as a monomer, react at particular temperature to form seed particles. The concentration of the monomer in the solution is critical to initiate the nucleation process. To expedite the growth process, precursor is quickly injected which exceeds the supersaturation limit of the solution. Consequently, rapid burst of nucleation of the particle erupts which reduces the concentration and bring it down below the supersaturation levels. Particle growth proceeds after that steadily by the diffusion of monomer species, this is called Ostwald ripening. Surface energy of a small nanoparticle is quite high (relative to total free energy), therefore crystal growth is thermodynamically favorable in order to minimize the total free energy of the crystal. So the number of particles are determined by the rapid injection step (supersaturation limit) while the size depends on growth process during Ostwald ripening stage.

Organic surfactant plays a vital role here in achieving monodisperse solution. Also, surfactants adhere to the surface of the particle controls the shape. Normally, Ostwald ripening would yield spherical nanoparticles due to its low energy configuration than its faceted counterpart. It is the surface energy of the different crystallographic planes that decides the growth direction. Due to energy minimization criteria, it is most likely results in isotropic growth. Anisotropic selective faceted growth requires the alteration of the crystal facet energy. This is achieved by selectively attaching organic ligands to the particular crystal facet, thereby reducing the growth rate of that facet and promotes anisotropic growth to achieve different nanostructured morphology. Figure 3.2 schematically shows the different stages of nanoparticle growth with time and dependence on monomer concentration.

3.1.3 Pulsed Laser Deposition (PLD)

Thin film deposition techniques can be divided into two broad classification – (i) Physical vapor deposition (PVD) and (ii) Chemical vapor deposition (CVD). PVD is done by directly using the material as target and deposited by vaporization followed by subsequent re-condensation on the substrate. Thermal/e-beam evaporation and sputtering are such examples. Material deposition by laser ablation is first demonstrated in 1960's after the development of ruby laser.¹¹ After that in 1980's Bellcore group showed that multifunctional layers of thin film can be deposited.¹² This spurred a widespread interest in the PLD technology, especially in the field of superconductivity. Chronological development of PLD has followed the advancement in the field of lasers. Advent of Q-switched lasers with very short pulsed duration made it possible to deposit films preserving the target stoichiometry. This feature made possible to deposit very complex multicomponent oxide thin films for superconductivity and ferroelectric devices.¹²

3.1.3 (a) Lasers

Electromagnetic energy interacts with the matter results in internal excitation processes. When a material is excited by means of electric, chemical or electromagnetic radiation, it perturbs the system by exciting atoms to excited state from the ground state. Excited atoms relaxes to the ground state in characteristic lifetime ($\sim 10^{-8}$ sec), called spontaneous emission. Einstein predicted that when a photon of particular energy is irradiated, excited atoms relaxes to the ground state simultaneously emitting a photon. This is known as stimulated emission. When the number of atoms in the excited state exceeds the number of atoms at the ground states, condition of population inversion is achieved. Then, external photon beam causes stimulated emission of a highly directional and monochromatic photon along with the incident photon. This forms the conceptual basis for the laser operation. Amplification of the stimulation emitted photon is what we know as Laser. Light emission process occurs in the active medium and high photon density is achieved by bouncing the photons back and forth in a cavity. Key attributes of a laser beam are high coherency, directionality, monochromaticity. Laser pulse energy densities can be very high depending on the excitation process and power used. Switching of laser pulses in time domain results in a narrow pulse width and remarkably high energy densities, capable of ablating the material. Laser pulses of narrow width with certain repetition rate is used to ablate the material and deposit thin films.

3.1.3 (b) Mechanism of Pulsed Laser Deposition

Basic PLD process is material ablation due to laser material interaction. Laser beam hits the target and rapidly boils the surface, thereby vaporizing the material. The vaporized material forms a directional plasma plume (of atoms, molecules, ions, electrons) after interaction with the laser energy. Figure 3.3 shows the schematic of the process.

Figure 3.2 Schematic of the pulsed laser deposition process.

Whole process proceeds in the following way –

Figure 3.3 Process flow of laser target interaction and plume formation mechanism.

As shown in Figure 3.3, laser beam hits the target and melts the surface rapidly followed by melting and vaporization. Melting from the surface quickly proceeds in the bulk (blue down arrow) and vaporization continues to occur at the surface (sky blue up arrow). Near surface vapor interacts with the laser energy and forms a plasma plume expanding vertically above the surface (shown in sky blue). The shape and extent of the plume depends on laser – target interaction volume and energy of the laser beam. Deposition is affected by many parameters *viz.* laser fluence, wavelength, pulse duration, repetition rate, target – substrate distance, background gas composition and pressure. All these parameters affect the growth conditions and the film quality.

PLD offers various advantages over other thin film deposition methods. Since the material is deposited by a highly directed plasma plume, material is congruently deposited at the substrate with very less contamination. There is no source of contamination unlike other process such as organic contaminants in CVD and unwanted impurities from crucible in evaporation. This makes PLD extremely useful for very precise and high purity film deposition. Also, chamber pressure can be tuned to achieve desirable growth rates so it spans the growth conditions like molecular beam epitaxy and evaporation without strict pressure requirements. However, there are few concerns regarding the film texture. Thermal shock causes the surface to literally break apart and deposits as particulate the substrate, known as splashing.¹³ Excessive superheating of the subsurface layers by the laser splashes spherical particle chunks at the surface. This is normally avoided by using particle filters or angled deposition. Dense and smooth targets are favorable to minimize this problem. Another concern is the uniformity. PLD uniformity zone is governed by the plume profile. Substrate rotation ensures uniform deposition throughout the substrate.

3.1.3 (c) PLD in Context of FeS₂

FeS₂ deposition has been very challenging in terms of quality and stoichiometry control. Both CVD and PVD deposition of pyrite thin films have been done before. However, impurities inherent to these approaches obscure the intrinsic defect studies of pyrite. Pulsed laser deposition offers excellent advantages to address these issues by providing better control on stoichiometry and minimal extrinsic impurities. Interestingly, PLD deposition of pyrite has never been done. This thesis project explores the opportunities to a new deposition technique for pyrite thin film deposition. Although, PLD deposition is well established for oxide films, deposition of sulfides are quite complicated due to the necessity of sufficient sulfur partial pressure. There are few reports of chalcogenide sulfide thin film depositions by PLD have been reported. This further corroborates that

it is feasible to deposit pyrite films by PLD. Natural pyrite crystals can also serve as a direct target to deposit film from it.

3.2 Characterization Techniques

3.2.1 X-Ray Diffraction (XRD)

One of the most profound discoveries in material science is the crystal structure study by X-ray diffraction. After the discovery of X-rays by German physicist Wilhelm Conrad Roentgen in 1895, X-rays were realized as important tool in many different areas of physics and medical science. When the light is allowed to pass through a slit and the wavelength is comparable to slit width, the light gets diffracted. The fact that light is an electromagnetic wave, it gets scattered through the slit producing spherical secondary waves that interferes constructively or destructively depending on the phase producing interference pattern. Von Laue realized that light is an electromagnetic wave and its wave nature can be exploited to get crystallographic details.¹⁴ Since the atoms are arranged in a periodic manner and the interatomic spacing is comparable to the wavelength of X-rays, X-ray diffraction is possible just as what diffraction grating does with the visible light. This further led to the study of various crystals structures by Bragg.

3.2.1 (a) Theory of X-ray Diffraction

Crystals are composed of atoms arranged periodically at the lattice sites. Diffraction of X-rays from lattice plane can be viewed as superposition of the scattered waves by the atoms. Wave scattering amplitude is a function of electron density, hence the resultant wave is a map of atomic positions and orientation. Due to lattice translational symmetry, intense X-ray diffraction peak is observed

along that direction. Incident X-ray beam is irradiated on the sample surface where it undergoes specular reflection from the parallel lattice plane composed of periodically arranged atoms.

Light reflected from the lower lattice plane travels an extra distance of $2d \sin \theta$. This introduces a phase difference and the reflected beam is interfered constructively or destructively depending on the phase difference. For constructive interference, phase difference has to be an integral number n of wavelength. The relation can be written as following

$$2d \sin \theta = n\lambda \quad \dots \dots \dots 3.2$$

The above relation is also known as Bragg's law.

3.2.1 (b) Lattice Planes and Scherrer Formula

For a 3- dimensional crystal system, there are 7 lattice types known as Bravais lattice. Crystal lattices are quantified by lattice constants a , b and c and corresponding reciprocal lattice vectors h , k and l . For a cubic crystal with a lattice constant of a , the two are related by

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad \dots \dots \dots 3.3$$

hkl are miller indices. Thus, if the direction and lattice constant is known, spacing between the plane can be calculated and vice versa.

Another important relation to calculate the crystallite size is the Scherrer formula given by the following relation

$$D = \frac{0.89 \lambda}{\beta \cos \theta} \quad \dots \dots \dots 3.4$$

Where λ is the wavelength of the X-ray used. In this thesis work, Cu K $_{\alpha}$ radiation ($\lambda = 1.54056$ Å) is used. β is the FWHM and θ is the diffraction angle for a particular (hkl) plane.

3.2.2 Raman Spectroscopy

Electromagnetic radiation interacts in a complex manner with the matter. When an electromagnetic wave is incident on the material, various process lead to the scattering of the wave. Incident wave of certain frequency scatters and comes out as same frequency (elastic scattering) and or different frequency (inelastic scattering). Inelastic scattering is known as Raman scattering. Molecules (or electron clouds) in the system are arranged at certain positions and marked by bond lengths. Electric field of the incident radiation interacts with the molecules electron cloud and results in a displacement of the ions forming a dipole. The dipole moment is caused due to the polarization from the electric field. Every molecule has specific dipole moment and hence the polarizability.

$$P = \alpha \vec{E} \dots\dots\dots 3.5$$

P is the strength of the dipole proportional to the electric field. Polarizability α is the material property and is a measure of how much that particular medium can be polarized and depends on the bond lengths, position of molecules and relative displacement by the electric field.

The change in the polarizability α is manifested by the scattering of incident light and the frequency of the out-coming light is changed or remains the same depending on the inelastic and elastic scattering. Bound atoms in a molecule vibrate with certain frequency called vibrational modes and have specific vibration energy. The relative change in the position during the vibration decides the degree of induced dipole moment, a necessary condition for the Raman

scattering. Raman scattering is usually weak in comparison to the fundamental (ν_0) light, hence it remained very difficult to observe the frequency shift in a bright background. Advancement in the field of laser proved to be extremely useful for Raman analysis. High intensity lasers made it possible to enhance scattering and increased Raman intensity.

Incident light of frequency ν_0 gets scattered and three distinct frequencies are possible. ν_0 , $\nu_0 + \nu'$ and $\nu_0 - \nu'$. When the frequency is unaltered ν_0 , it is known as Mie or Rayleigh scattering. However, due to inelastic scattering resultant frequency may decrease $\nu_0 - \nu$ (Stokes shift) or increase $\nu_0 + \nu$ (anti-stokes shift). This inelastic scattering is referred to as Raman scattering. Different vibrational modes give characteristic Raman signal which is like a finger print of the particular bond present in the specimen. Thus Raman is used to identify the vibrational modes present in the material characteristic of chemical bonds present. Since the modes are due to the relative position of the atoms, group theory provides information of the possible modes on the basis of symmetry.

3.2.3 Optical Absorption

3.2.3.1 Beer-Lambert's Law

When a light passes through a material, it undergoes absorption, reflection and transmission. So the light in and light out from a material is different in terms of intensity and wavelength range. When a light of intensity I_0 passes through a material, some amount of light is absorbed depending on the absorbance of the material A and light coming out is I , then the three are related by

$$A = \log_{10} \left(\frac{I_0}{I} \right) \quad \dots \dots \dots 3.6$$

Figure 3.4 I_o is the intensity of light incident on the specimen and I_o is the intensity of transmitted light that comes out after absorption and reflection.

This implies that if the light incident and coming out becomes equal ($I_o = I$), then the absorption at that particular wavelength is zero. Spectrometer is used to conduct these measurements. Sometimes, the absorbance is plotted is from 0 to 1 or in percentage. It is important to recognize that absorbance might be exceeding 1 if more than 90 % of light is absorbed. This is due to the logarithmic scale, which is 1 if the ratio I_o/I is 10 % (this is when absorption is 90 %) and 0 when absorption is 100 %.

3.2.3.2 Spectrometer

Optical absorption measurements are performed by UV-Vis absorption spectroscopy. A spectrometer is normally used to measure light intensity as a function of wavelength. Schematic diagram of the interior components are shown in Figure 3.5

Figure 3.5 Schematic of the interior components of a spectrometer for measuring optical absorption, reflection and transmission.

Lamp is used to cover UV-visible wavelength range from 200 nm to 2000 nm. Normally this is achieved using a combination of light sources to cover the full wavelength range. Grating splits the light to different wavelengths at different angles. Rotating the grating allows to focus selective wavelengths on the slit and rendered on the rotating disk where the light splits in two parallel channels. One is focused on the sample while the other channel is used as a reference. Subtraction of the reference signal from the sample gives absolute light intensities from the sample. The final signal is then fed to the computer where the data is displayed and analyzed.

3.2.3.3 Indirect and Direct Bandgap Semiconductor

Energy bands in semiconductors are separated by a forbidden energy region, known as the bandgap of the material. Energy separation from valence band maxima and conduction band minima (bandgap) corresponds to the UV-Visible-IR part of the energy spectrum. Optical absorption spectroscopy is the most commonly adopted technique to determine the bandgap of the semiconductor. Photons of energy equal to or/and higher than the bandgap absorbs by the material and excites carrier from valence band maximum to conduction band minimum. Nature of optical transition depends on the band structure of the material. Position of the valence and conduction band in k-space decides whether the material is direct band or indirect band semiconductor. Figure 3.8 shows the band structure of a direct and indirect bandgap semiconductor.

For a direct band semiconductor, valence and conduction band edges lie on the same wavevector k - value so electron is directly excited to conduction band by a photon of energy $\hbar\nu$. While for an indirect band semiconductor, valence and conduction band lie at different wavevector k - value. Since the photon doesn't carry momentum, energy-momentum conservation requires the momentum to be provided by lattice phonons of energy $\hbar k$. Hence, either a phonon is absorbed or

emitted in an indirect transition process. The transition from one state to the other are governed by the transition matrix for dipole transition. The transition rules are formulated as Fermi Golden rule. Indirect transitions are not as efficient as direct transition.

Absorption coefficient is related to the bandgap of the material by Tauc relations given by the following

$$\alpha(\lambda) \propto A (E_{\text{photon}} - E_g)^{1/2} \dots 3.7 \quad (\text{Direct bandgap})$$

$$\alpha(\lambda) \propto B (E_{\text{photon}} - E_g)^2 \dots 3.8 \quad (\text{Indirect bandgap})$$

Extrapolation of plot of $\hbar\nu$ vs $(\alpha\hbar\nu)^{1/2}$ and $\hbar\nu$ vs $(\alpha\hbar\nu)^2$ gives the value of the bandgap for indirect and direct bandgap semiconductor respectively.

3.2.4 Electrical Measurements

3.2.4.1 Hall Measurements

Determination of carrier type and mobilities are of extreme importance in solar photovoltaics. Hall measurement is based on Hall effect in semiconductors after Edwin Hall in 1879. The phenomena observed by Hall became the one of the most fundamental basis of semiconductor physics. Hall noticed that the current flowing through a wire experiences a force due to magnetic field. Precisely, if a magnetic field is applied perpendicular to the flow of the electric charges, then the charge carriers are deflected in a transverse direction due to Lorentz force. Thus a transverse electric field is developed (and hence a voltage, known as Hall voltage). The field developed is proportional to the applied magnetic field, giving rise to magnetic field dependent resistance called magnetoresistance. Figure 3.6 schematically shows the Hall effect.

Figure 3.6 Schematic of Hall effect in a semiconductor.

Hall coefficient is defined as, $R_H = -1/ne\mu$

Where n is the carrier concentration, e is the electronic charge and μ is the mobility. The sign of Hall coefficient is decided by the type of charge carrier. This is how charge carrier type is determined. However, care must be taken to interpret the Hall sign. For example, when the transport is not simple diffusive but hopping, Hall interpretation is not straight forward. Also, it is complicated to interpret Hall data when there is band inversion or accumulation layers present at the semiconductor surface. The reason behind is that mobility cannot be simply written as

$$\sigma = n_n e \mu_n \dots\dots\dots 3.9$$

But written as, $\sigma = n_n e \mu_n + n_p e \mu_p \dots\dots\dots 3.10$

Mobility then becomes a function of both electron and hole mobility. If inversion/accumulation layers are present, it requires more than just a classical physics to describe that.

For iron pyrite, this is an extremely important consideration. This may be the possible reason why carrier sign determination remained controversial for a long time for pyrite samples. Recent investigations seem to correlate with these

observations by providing direct experimental evidence of surface inversion layers in pyrite single crystals.

3.2.4.2 Electrical Transport Measurements

Electron transport is of prime importance in understanding device performance and defect physics in a semiconductor. Resistivity change as a function of temperature is characteristic to particular scattering mechanisms in the material. Different defects play dominant role in different temperature regimes. Hence, temperature dependent resistance measurements are performed to get insights about electrical charge transport. Conventional (band to band) transport in semiconductor can be described as diffusive with some activation energy. Resistivity and temperature is related by the following relation

$$\rho = \rho_o \exp(-E_A/k_B T) \quad \dots \dots \dots 3.11$$

ρ is the resistivity, E_A is the thermal activation energy. Transport occurs through the diffusion of carriers due to vacancies/defect concentration. Thermal energy provides enough energy to overcome the diffusion energy barrier. For a clean semiconductor, carriers are activated from band to band and the E_A corresponds roughly to the bandgap of the material.

Defects in semiconductor lead to localized defect states giving rise to hopping transport. In disordered semiconductors, many such localized defect states are present. The resistivity dependence on temperature changes in a following way

$$\rho = \rho_o \exp\left(\frac{T_o}{T}\right)^{1/d+1} \quad \dots \dots \dots 3.12$$

ρ is the resistivity, ρ_o is a weak temperature dependent pre-exponential factor (value of ρ at $T \rightarrow \infty$) which depends on the electron-phonon interactions. d is

the exponent of dimensionality of the system. T_0 is the characteristic temperature. The above transport is known as Mott-variable range hopping (Mott-VRH). The conduction is through phonon assisted hopping of electrons to localized states. In deriving the above relation, the density of states is assumed to non-zero and constant at the fermi level within the thermal energy interval between localized states.

3.2.5 Thermoelectric Measurements

3.2.5.1 Theory of Thermoelectricity

Thermoelectricity deals with the relationship between heat (thermal energy) and electricity (electrical energy). The two quantities are related to each other and variation in the one triggers the change in the other. There are three types of thermoelectric effects: Seebeck effect, Peltier effect and Thomson effect.

Seebeck effect was observed by German physicist Johann Seebeck in 19th century. Seebeck noted that when a junction between two metals (Copper and Bismuth) is made and one of the junctions is preferentially heated, it caused a deflection in the magnetic needle placed in the vicinity. This discovery was serendipitous as he was just looking for relation between heat and the electricity. Later only he realized that the deflection in the magnetic needle was caused due the current produced by the temperature difference between the metal junctions. This became what we know today as Seebeck effect. So in a typical thermopower measurement, Seebeck coefficient is measured by heating one of the junctions and monitoring the voltage developed across it. Figure 3.7 shows the open circuit configuration to measure Seebeck coefficient.

Figure 3.7 Schematic diagram of the thermopower measurement at open-circuit configuration. Wire 1 and 2 are made of with different metals, ΔV_{12} is the voltage developed due to temperature gradient of ΔT .

Measurement in short-circuit configuration is not usually done in order to avoid the discrepancy caused by the resistive losses during the current flow.

Origin of Seebeck effect is twofold. One contribution comes from the fermi level dependence on the temperature given by the following Fermi-Dirac equation

$$f(E) = \frac{1}{e^{\frac{E-\mu}{k_B T}} + 1} \dots\dots\dots 3.13$$

As the temperature varied, Fermi level changes and consequently a potential is developed causes the current to flow. Second contribution comes from the equilibrium which is established in a semiconductor due to drift-diffusion balance. The internal field that balances the diffusion and drift components of the electric current results in a net current density which is sensitive to the temperature change. Final thermoelectric potential is the sum of both the contributions. For an n-type semiconductor under non-degenerate approximation yields the following relation for the Seebeck coefficient

$$\frac{\Delta V}{\Delta T} = S = -\frac{k_B}{e} \left[r + \frac{5}{2} + (E_C - E_F)/k_B T \right] \dots\dots\dots 3.14$$

$E_C - E_F$ is positive, hence for n-type semiconductor Seebeck coefficient is negative. For p-type semiconductor, the term $E_C - E_F$ is replaced by $E_V - E_F$. E_V

– E_F is negative, hence for holes Seebeck coefficient is positive. So from the above arguments, the sign of the Seebeck coefficient essentially denotes the direction of the current flow (However, the above analysis is for open-circuit configuration for which the current flow is zero). For p-type semiconductor, the electron current flows from cold end to hot end while for n-type semiconductor, the electron current flows from hot end to cold end.

For degenerate semiconductor, equation 3.8.2 modifies to following equation

$$S = \left(r + \frac{3}{2}\right) - \frac{k_B^2 \pi^2 T}{3eE_F} \quad \dots \dots \dots 3.15$$

3.2.5.2 Measurement Details

Thermoelectric measurement performed in this work are on a custom made system designed for room as well as temperature dependent thermoelectric measurements up to 150° C. Full details of the equipment is described in the thesis of Nate Miller.¹⁵ The sample was placed across the Cu blocks on top of Indium foil to ensure good thermal contact. Cu blocks are resistively heated by the temperature controller which takes the input from the Lab-View program. Figure 3.8 shows the photograph of the experimental set-up

Figure 3.8 Photograph of the thermoelectric measurement set-up. Sample is placed across two Cu heating arms. Temperature readout is done by RTD and the thermocouple simultaneously and fed to the temperature controller operated by a Lab-View program.

To conduct temperature dependent measurements, the whole assembly is enclosed in a vacuum chamber connected to a liquid nitrogen Dewar container.

3.2.6 Rutherford Backscattering Spectroscopy

Rutherford backscattering spectroscopy (often called as just RBS) is a strong surface analysis technique for in-depth composition analysis of thin films. The principle is based on elastic and inelastic scattering of charged particle by the element. To get the in-depth compositional details from a sample, a high mono-energetic probe ion beam is bombarded on to the material surface. Typical probe beam is He ion with energy range in MeV. The energetic beam then interacts with the elements present in the sample and gets scattered in different directions and energies depending on the element mass and concentration. RBS analyzes the backscattered ions from the specimen. A solid state silicon detector is used to analyze the backscattered ions position at a particular angle with respect to incident beam angle.¹⁶

High energy He^{2+} ions are produced by NEC model 5SDH Pelletron tandem accelerator which is then collimated to the sample chamber compartment by magnetic coils. RBS Si detector produces electron hole pairs due to striking backscattered ions. Electrical signal is directly proportional to the energy of the backscattered ions. RBS is extremely sensitive up to ppm levels for the heavy element. For lighter elements however, RBS is less sensitive and other detectors such as electron recoil detection (ERD) is used. RBS is a non-destructive technique to quantitatively analyze in-depth elemental composition without the need of reference sample. Figure 3.9 shows the RBS measurement schematic.

Figure 3.9 Schematic diagram of Rutherford Backscattering measurement assembly.

3.2.7 Optical Pump Probe Spectroscopy

Optical pump probe spectroscopy is the most versatile ultrafast spectroscopy tool to investigate charge carrier dynamics in a semiconductor. Laser beam is split into two beams, pump pulse and probe pulse. Pump pulse of particular wavelength and power density is used to excite carriers to the top energy levels of the semiconductor. Probe pulse is sent with a time delay of ΔT (femtosecond to microseconds) to monitor the change in the optical absorption of the semiconductor. Pump pulse excites all the carriers from the ground state to the excited states, these excited carriers decay to low lying energy levels with certain lifetimes. Keeping track of the carrier population and lifetimes at the energy levels gives charge carrier dynamics within the material.¹⁷ This is achieved by

measuring transient absorption spectra (TA). Transient absorption is the temporal change in the absorption of the material after pump excitation. When all the carriers from the ground state are excited, ground state carriers are bleached and hence the change in absorption is negative. So negative ΔA corresponds to photobleaching. When the carriers are excited to higher energy levels to certain energy level under probe, the ΔA signal is positive and corresponds to photoinduced absorption (PIA). It is important to excite carriers uniformly so that the probe signal corresponds to actual carrier decay but not due to other optical processes. The lifetime of charge carriers τ is then obtained by fitting the decay curve with the exponential decay function, given as following:

$$y = A_1 * \exp\left(-\frac{t}{\tau}\right) \dots \dots \dots 3.16$$

Probe pulse diameter is much smaller than the pump pulse to make sure that the signal is collected from the area of uniform optically excited carrier generation. Figure 3.10 shows the schematic of the carrier excitation from pump and carrier relaxation processes probed in semiconductor in typical pump probe measurement

Figure 3.10 Schematic of a typical pump probe measurement set up.

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Chapter 4

Iron Pyrite Thin Film (FeS₂) Prepared by Spray Pyrolysis

This chapter discusses the production of iron pyrite thin films by spray pyrolysis. In principle, spray pyrolysis is a method where precursor chemicals are sprayed onto a heated substrate to evaporate the solvents and react the remnants to achieve a film of the particular compound. The principles of the process are described in Chapter 3. The spray pyrolysis process has been used even to deposit complex compounds such as CIS,¹ CZTS,² CIGS³ etc. successfully. Similar approach is adopted here to prepare pyrite thin films. The choice of water as the solvent makes the process more environmentally friendly. Optical and electrical properties of the film are studied in detail. Temperature dependent electrical transport study is performed to shed light on defect mechanism. Catalytic activity of pyrite is examined as counter electrode in DSSC cells and performance is evaluated.

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4.1 Film Fabrication Procedures

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (MW 270.30 g/mol) and thiourea ($(\text{NH}_2)_2\text{CS}$) (MW 76.12 g/mol) were used as Fe and S precursor respectively, and de-ionised (DI) water as the solvent. 0.1M solution of iron chloride (1.35 g in 50 ml of DI water) and thiourea were first prepared (0.38 g in 50 ml of DI water). The two solutions were mixed in more DI water in Fe:S atomic ratio of 1:6 by weight to get the spraying solution. For example, a total of 50 ml spraying solution contains 7 ml of 0.1 M $\text{FeCl}_3 \cdot \text{H}_2\text{O}$ solution, 4.2 ml of 0.1 M thiourea solution and 38.8 ml of DI water. Ratios of Fe: S precursor less than 1:6 were also tried but this always ended up with incomplete conversion of the films to pyrite in the final product. Ratios more than 1:6 result in a dark and dense solution and formed particulates on the surface after spraying which could be visually seen with naked eye. Three substrates were used for the study namely quartz, glass and FTO coated glass. The substrates were cleaned thoroughly with acetone, IPA and rinsed with water and blow dried by air gun before deposition. Substrates were then mounted on a metallic plate which was placed at the center of the hotplate. Spraying of the precursor was started once the substrate reached the required spray temperature of 350°C . Flow of nitrogen carrier gas was manually adjusted to achieve a spray of fine droplets in the form of a uniform mist. Too high or too low flowrates were not beneficial to achieve a uniform deposition. A steady spray rate was maintained by manual adjustment of the nozzle of the spray gun. The nozzle was continuously scanned across the surface for full coverage of the deposition area *via* a computer controlled robotic spray arm. The movement of the robotic spray arm was controlled by computer program to minimize the cooling effect arising from the spray depositing on the hot substrate while achieving a uniform coverage of the area. Substrate temperature was maintained at the optimum value of 350°C throughout the spraying process. Film thickness was varied by changing the duration of the spray. Normally, spraying 50 ml of solution for ~ 45 mins yield a film of thickness of

around 200 nm. The schematic of the spraying process and the subsequent sulfurization process is shown in Figure 4.1.

The sprayed films were annealed subsequently to fully crystallize the compound and complete the reaction. Annealing was done in a sulfur atmosphere to maintain the stoichiometry as sulfur loss is common in pyrite during heat treatments. Optimization of the annealing sulfurization temperature was done after annealing trials in the temperature range 300° C to 600° C for 60 minutes to 30 minutes. For device fabrication, the sulfurization conditions chosen were 400° C for 30 minutes. Sulfur powder was kept in the tube along with the sample and an argon carrier gas was slowly flown ~ 20 sccm through the tube during the annealing process.

Figure 4.1 Schematic of the spray pyrolysis and sulfurization process set up and relevant parameters.

4.2 Results and Discussions

4.2.1 Crystal Structure and Phase Analysis

As-deposited films on the hot substrate were found to be amorphous and light brown in color. Substrate temperature variations did not show any crystallization in the films. The as-sprayed amorphous films were mostly Fe-S-O complexes as chemical analysis showed the elements Fe, S and O to be distributed uniformly over the film. Figure 4.2 (a) shows the XRD and Raman spectra of the films in the as-sprayed condition and after sulfurization at different temperatures.

Figure 4.2 (a) XRD and (b) Raman spectra of as-sprayed and sulfurized films at different temperatures.

From Figure 4.2 (a), no XRD peaks are observed for as-sprayed films, indicating their amorphous nature. Sulfurization annealing causes crystallization and diffraction peaks begin to appear in XRD spectra. At 400° C – 500° C sulfurization temperatures, all the peaks obtained can be indexed to the cubic FeS₂ pyrite phase as shown in Figure 4.1(a). None of the peaks corresponding to the marcasite phase are detected.

The lattice parameters were calculated from XRD peak fitting using Scherrer formula as explained in Chapter 3.

Fitting of (200) peak (centered around 32.9°) with a Lorentzian profile is used to extract FWHM (β) and plugged in the Scherrer's formula to estimate crystallite size. Maximum crystallite size for the sulfurized films ranges from 30 nm – 50 nm. Lattice parameter calculated from XRD spectra yields $a = 5.419 \text{ \AA}$ which is close to the reported value for high quality pyrite sample ($a = 5.417 \text{ \AA}$).⁴ Sulfurization temperature and time influence the phase purity and crystallinity of the film. We found that the temperature range 300° C to 500° C was favorable for pyrite formation. Below 300° C, the temperature was not high enough to drive the reaction while above 500° C, pyrite starts decomposing. The best pure phase films were obtained when sulfurized in the temperature range 400° C – 500° C for 30 mins to 60 mins. However, since XRD is not sensitive to detect impurity contents < 2 % XRD evidence alone is insufficient to prove the phase purity of the pyrite films.

Raman spectroscopy is an alternative, but a very sensitive technique to detect different phases present in the film. Raman spectroscopy is sensitive to the crystallinity and any ordering in the sample, and would give rise to Raman signal. As-sprayed films (Figure 4.2 b) show no Raman activity confirming the amorphous nature of the films shown by XRD. Pyrite Raman signals appear from 400° C indicating crystallization. No signals corresponding to the vibrational modes of marcasite or any other Fe-S phase is observed. Because of the higher sensitivity of the Raman technique, Raman spectra proves the phase purity of sulfurized pyrite thin films. Three peaks observed are shown in Figure 4.2 (b) corresponding to pyrite vibrational modes. While no other peak related to any other phase is observed. The three peaks at 343 cm⁻¹, 379 cm⁻¹ and 429 cm⁻¹ correspond to A_g, E_g sulfur dumbbell stretching modes and T_g (3) vibrational

mode respectively.⁵ Group theory calculations predict 5 lattice vibration modes of pyrite at Brillouin zone Γ point ($k = 0$) as following –

$$\Gamma = A_g + E_g + T_g (3) + A_u (2) + E_u (2) + T_u (6) \dots \dots 4.1$$

Five modes A_g , E_g and $T_g (3)$ are Raman active modes. $A_u (2)$ and $E_u (2)$ are infrared active modes and $T_u (6)$ correspond to acoustic phonon mode.⁶ Out of five, three Raman modes clearly observed in Figure 4.2 (b) while the two other Raman modes related to $T_g (1)$ and $T_g (2)$ are not usually observed due to light extinction at room temperature and low scattering cross-sections.⁷ The possible vibrational modes are shown as schematic in Figure 4.3.

Figure 4.3 Vibrational modes corresponding to (a) Infrared active and (b) Raman active mode.

From combined analysis of XRD and Raman, crystallinity and phase purity of sulfurized thin films are confirmed. This is used as standard metric to evaluate quality of synthesize pyrite in the lab for further characterization and device application.

4.2.2 Surface Morphology and Effect of Sulfurization

Surface morphology changes with annealing treatment of the film. As-sprayed films show no signs of grain formation but look like a continuous globular, “cloud-like” matrix. Annealing treatment leads to grain nucleation and growth leading to a polycrystalline film finally. The final grain size increases as the temperature is increased. Figure 4.4 shows the scanning electron micrographs (SEM) showing the surface morphologies of the films.

Figure 4.4 Top view SEM of (a) as-sprayed film and sulfurized at (b) 300° C, (c) 400° C, (d) 500° C and (e) 600° C. (f) tilt- view cross-section SEM of films sulfur annealed at 500° C. Film thickness is approximately 400 nm.

Notably, the sulfurized films are rougher than the as-sprayed film. Growth kinetics governs the film morphology, orientation and roughness. We found that smoother films could be obtained by slower deposition rates. Whether one requires a rough or smooth film generally depends on the application. The grain size obtained varied somewhat but with an average size of about 50 nm.

4.2.3 Surface Chemical Analysis

To investigate the surface elemental composition of the pyrite films, X-ray photoelectron spectroscopy was utilized. Figure 4.5 shows the wide scan of the sample which shows peaks from Fe, S, C and O. Synthetic precursors contain carbon as a contaminant which might be the reason for detecting C-1s peak. O is also a common surface contaminant as the spraying process was done under ambient conditions. Even exposure to atmosphere after sulfurization could be sufficient to cause oxygen to adsorb on the surface of pyrite.

Figure 4.5 Wide scan XPS spectra of FeS_2 film sulfurized at 400° C for 30 mins.

To gain deeper insights about the binding energies, slow scans of Fe 2p, S 2p and O 1s peaks were scanned and the results are shown in Figure 4.6 (a), (b) and (c) respectively.

Figure 4.6 XPS scans of (a) Fe 2p, (b) S 2p and (c) O 1s levels for sample sulfurized at 400° C.

In Fe 2p spectra, two predominant peaks are observed at 707.5 eV and 720.0 eV corresponding to Fe 2p_{3/2} and Fe 2p_{1/2} doublet splitting due to spin-orbit coupling. These binding energies (BE) are in agreement with the Fe (II)-S bond.⁸ The small shoulder observed at the high energy side near 709.1 eV is attributable to the surface defects or related to Fe (III)-S bond formation at the surface.⁹ This high energy tail is reported to be observed even in single crystals cleaved inside the UHV XPS chamber. This indicates the oxidizing nature of the pyrite surface causing monosulfide species to form. No peaks for binding energies corresponding to Fe oxide FeO (708.4 eV) and Fe₂O₃ (709.8 eV) are observed.¹⁰ Two peaks are observed for sulfur S 2p at 162.9 eV and 162.0 eV respectively in Figure 4.6 (b). The major peak at 162.9 eV corresponds to persulfide S₂²⁻ binding energy in FeS₂.¹¹ Deconvolution of the spectra shows a small peak at 162.0 eV which is attributed to the disulfide ions present at the surface.^{12,13} Other peak at 164.5 eV is due to the molecular polysulfide (S_n²⁻) species. Condensed sulfur on the surface is a source of polysulfides and such condensation can be prevented by careful control of sample cooling and its position in the furnace relative to the sulfur source. The peak at 531.6 eV in O 1s spectrum of Figure 4.6 (c) is due to hydroxides. Usually, O 1s binding energy is around 529 - 530.1 eV for oxides,^{14,15} 530.9 - 532.1 eV for hydroxides like OH,¹⁶ and 532.3-533.8 eV for water adsorbed at the surface.¹⁷ So the observed peak at 531.6 eV is most likely to be associated with hydroxides on the surface. On the basis of XPS analysis, it is evident that film composition is predominantly equivalent to that of pyrite with some surface defects.

Figure 4.7 Rutherford backscattering (RBS) spectra of the sprayed and sulfurized thin films deposited on quartz substrate.

Stoichiometry of sprayed and sulfurized thin film was evaluated using RBS analysis. Figure 4.7 shows the RBS spectrum of a 200 nm film deposited on quartz substrate. Two peaks corresponding to Fe and S can be seen. Curve fitting of the RBS data yields a good fit for Fe: S ratio of 1:2 which is stoichiometric for pyrite. The background signal below Channel 600 is from the substrate.

4.2.4 Optical Properties

Optical absorption by a sample is indicative of the distribution of density of states in the material, and hence, can be used as a signature of energy bands. High optical absorption is a characteristic trait for pyrite. The UV-Vis absorption spectra were measured for as-prepared and sulfurized films at different temperatures using integrating sphere. Figure 4.8 (a) compares the optical absorption of the as-sprayed film and those films sulfurized at different temperatures for 30 mins.

Figure 4.8 Optical absorption spectra of (a) as-sprayed and sulfurized film at 300° C, 400° C and 500° C (b) 200 and 400 nm films sulfurized at 500° C.

As the sulfurization temperature is increased, the band edge shifts towards higher wavelengths (redshift), as shown in Figure 4.8 (a). This goes back to the previous discussion on as-sprayed amorphous film. The band gap of an as-sprayed film resembles that of iron oxide. Sulfurization annealing converts any iron oxide that may be present in the as-sprayed film to pyrite. The optical absorption spectra for 400°C and 500°C, annealing look typical of a pyrite material i.e. high optical absorption at visible spectrum and the band edge in IR region.^{18,19} It should be noted however that a significant band tailing is observed in almost all the samples. This had been debated extensively in the field. Classic chalcogenide glasses also exhibit such absorption features.²⁰ Band gap reported for pyrite is usually in the range 0.90 eV to 1.10 eV. Most of these reports are based on optical measurements.²¹

Figure 4.9 (a) Absorbance vs Energy, (b) Ln A vs E and (c) band gap analysis from Tauc plot for pyrite thin film sulfurized at 400° C for 60 mins.

Strong absorption onset observed for energy higher than 1 eV (Figure 4.9(a)) corresponds to band-to-band transition. Note that optical absorption does not increase abruptly at the band edge which is consistent with the proposals in the literature that the band gap of iron pyrite is indirect. Conservation of momentum requires the participation of phonons in the optical excitation. From figure 4.9 (a) distinct absorption edges can be seen (~ 1 eV and 2.4 eV) for the pyrite film sulfurized at 400° C. Below 1 eV energy, an exponential band tail feature is observed. Below the band gap exponential band tails are convoluted with the density of states giving rise to optical excitations with the states adjacent to the band gap. The tail is called the “Urbach tail”.²² Density of states in the energy tail is correlated to gaussian potential associated with the disorder. Hence the electron energy follows the exponential distribution in these states. Since the disorder in a material is a result of static or dynamic fluctuations of its potential due to defects and short range order, the slope of the Urbach tail is directly correlated to the density of defects.²³ Lower Urbach tail (slope Ln A vs E) from Figure 4.9 (b) indicates high degree of disorder in the material. Band gap estimation is done using Tauc plot analysis. For band to band transition, optical absorption equation can be written as

$$h\nu\alpha = B (h\nu - E_g)^{1/n} \dots\dots\dots 4.2$$

where, $n = 2$ for direct optical transition and $n = 1/2$ for indirect optical transition; B is the optical transition matrix element coming from the Fermi golden rule. From Figure 4.9 (c), the band gap value appears to be ~ 1.04 eV. This value is within the range of commonly reported band gap values for pyrite. However, the value in this case fits best with the direct optical transition rather than indirect. This finding is not surprising as indirect band gap semiconductors with high density of defect states have shown to exhibit direct optical transition.²⁴ This can be understood in terms of basic momentum conservation requirements. In indirect semiconductors, the electron transition to higher energy levels occurs at different k value unlike in direct semiconductors where the transition occurs at the same k value of conduction band minimum (CBM) and valence band maximum (VBM). This requires a phonon momentum of $\hbar k$, in addition to a photon, to conserve the momentum. When the defects near the band edge form a defect band, optical transition could directly occur from valence band to defect band. This relaxes the momentum conservation requirement from phonons and material absorption behaves like in a direct gap semiconductor. This can be understood by following relations.

$$h\nu = E_c - E_v \quad , \text{for direct transition} \dots\dots\dots 4.3$$

$$h\nu + \hbar k = E_c - E_v \quad , \text{for indirect transition} \dots\dots\dots 4.4$$

4.2.5 Charge Transport Properties

Electrical properties of the pyrite films were studied by Hall measurements performed in Van der Pauw configuration. Aluminium contacts were thermally evaporated at the corners serving as electrical contact pads. Choice of Al as contact was entirely on the basis of work function matching to get a good ohmic

contact. All measurements were performed in ambient and as well as in vacuum. Special care is required to make contacts at the corner to avoid any boundary effects. Table 4.1 shows the results of various electrical parameters measured by this method.

Table 4.1 Electrical parameters obtained from Hall analysis of pyrite film annealed at 400° C for 30 mins.

Parameter	Without Vacuum	In Vacuum
Resistivity (Ohm*cm)	0.54	0.58
Mobility (cm²/V-s)	4.22	2.12
Carrier density (cm⁻³)	2.71 x 10 ¹⁸	5.04 x 10 ¹⁸
Hall Coefficient (cm³/Coul)	2.30	1.23
Sheet resistance (Ohm/cm²)	27235.1	29138.9
Type of carrier	Holes	Holes

Generally p-type conductivity is observed for pyrite thin films. However, to the contrary, pyrite crystals behave differently showing n-type behavior in most if not all the cases. This perplexing behavior is believed to originate from the complex surface physics of pyrite. The n-type crystals with a strong fermi level pinning at the surface due to surface defects could also show the effect similar to the behavior of thin films.²⁵ Thin Films could be imagined to be composed of many such pinned interfaces leading to a high hole concentration and consequently a p-type behavior. The mobility values obtained in the current study is comparable, and in some case better than, the high quality pyrite films fabricated before by the researchers.⁵ Although the Hall measurements show p-type conductivity, the interpretation can be erroneous due to low value of Hall co-efficient. There exists a lot of confusion in the literature in identifying the carrier type in the samples.²⁶ Also, Hall measurement is a surface sensitive technique and dominated by surface conductivity. Thermoelectric Seebeck measurement, on the other hand, is a bulk sensitive technique as Seebeck

coefficient is diffusion driven. Seebeck measurements were also performed in this project to identify the charge carrier type. At room temperature, a positive Seebeck coefficient of about 35 $\mu\text{V/K}$ was obtained. This supports a p-type conduction mechanism in the film. Figure 4.10 shows the temperature dependent Seebeck coefficient for the pyrite film.

Figure 4.10 Temperature dependent Seebeck coefficient measurements for sprayed and sulfurized iron pyrite thin films on quartz substrate.

Linear correlation of the Seebeck coefficient with the temperature in Figure 4.10 suggests the behavior of a degenerate semiconductor (refer to Seebeck coefficient description in Chapter 3). For PV application, ideal carrier density values should be in the range $10^{14} - 10^{17} \text{ cm}^{-3}$ for efficient charge collection and good voltage. The value of 10^{18} cm^{-3} obtained in this case (by Hall measurement) is certainly on the higher side and lower values are desirable. Although the efforts made to reduce the carrier density are not successful yet, these values are low among the thin film class with only few exceptions.

Such high carrier density and relatively low band gap of pyrite ($\sim 1 \text{ eV}$) pushes the semiconductor to the degenerate limit (metal-like). Schottky devices made depositing gold (which has high difference in work function with pyrite) on pyrite but an ohmic behavior was observed instead of rectification, which should have

otherwise observed. Device configuration to make Schottky barrier cell is shown in Figure 4.11 below

Figure 4.11 Schematic of the Schottky device made from spray pyrolyzed film on FTO and Au top contact to make Schottky barrier.

Regardless of what metal was used, the I-V response exhibited an ohmic behavior. This phenomenon is anticipated for semiconductors with their Fermi levels pinned at the surface. At equilibrium, the surface states are filled by bulk carriers leading to band bending at the surface. The apparent electrochemical potential of the bulk is then dictated by the surface potential regardless of the actual value of the bulk electrochemical potential (Fermi level). So when a contact is made with different work function metals, Fermi level position of the semiconductor remains pinned and as a consequence I-V response becomes insensitive to the metal interface.²⁷

Figure 4.12 Ultraviolet photoelectron spectra (UPS) of the pyrite film sulfurized at 400° C and the measured work function.

Fermi level position for pyrite thin films were measured by ultraviolet photoelectron spectroscopy (UPS) in this project. In this method, a sample was irradiated with low energy X-rays and ultraviolet rays were used to eject electrons near the Fermi level. As shown in Figure 4.12, work function of 4.74 eV is obtained and the energy position lies closer to the valence band edge, consistent with p-type behavior. This value is close to the work function measured by different techniques and on different samples.²⁸⁻³⁰ The insensitive Schottky behavior and ubiquitous work function values for different sample give strong evidence of Fermi level pinning in pyrite.

Electronic defects in a material influence the temperature dependence of its conductivity in a specific way as the scattering of electrons by defects impacts the conductivity. Hence, the resistance variation with temperature will reflect the characteristics of the effects of temperature on defects, elucidating the defect scattering mechanism that is limiting the conductivity at every temperature. To gain deeper insight on the conduction mechanism and the impact of crystal defects on pyrite, electrical transport from room temperature to 10 K was measured in this project.

Figure 4.13 Electrical transport measurements of pyrite film deposited on quartz substrate. (a) Ln R vs T, (b) Ln R vs 1/T and (c) R fitted with T^{-1/2} (ES-VRH) and T^{-1/4} (Mott-VRH) fit.

In a normal conductor, the I-V relationship is linear following Ohm's law. In a perfect crystalline material with no lattice defect, current would increase proportionately with voltage. However, in practice it doesn't happen because lattice defects do exist, and due to various electron-electron, electron-phonon scattering processes, the I-V relationship is non-linear and the conductivity becomes the function of the electric potential.³¹ The operating carrier scattering mechanism depends on the temperature. Theory of disordered semiconductors deals with different transport mechanisms responsible for peculiar dependence of resistivity (R) on temperature (T). This dependence changes in a complex manner in a microscopically inhomogeneous specimen. Conventional band to band transport is a thermally activated process, exciting the carrier from donor or acceptor level to conduction or valence band. The energy required in this process is called "defect activation energy". For a semiconductor in the intrinsic regime (high temperature and low doping concentrations), the defect activation energy is roughly half of the value of the band gap of the semiconductor.³¹ However, in a low band gap disordered semiconductor, the electron experiences potential traps created by defects and could get localized at the defects. This is well explained in the theory of charge carrier localization by Anderson.³¹ Defects and the randomness in a material generate inhomogeneity in the distribution of local electric field and then carrier transport occurs *via* phonon mediated or quantum mechanical "hopping" process. Figure 4.13 (a) shows the complete resistance *vs* temperature plot for pyrite thin film. Typical semiconducting feature is obtained with high conductivity at the room temperature. Three distinct regimes can be identified in this figure –

- (1) Thermally activated conduction (TAC) regime (270 K – 400 K),
- (2) Mott-Variable range hopping (VRH) (65 K – 255 K)
- (3) Efros-Shklovskii variable range hopping (ES-VRH) (16 K – 35 K).

Analysis of TAC regime could be done by fitting the Arrhenius equation (Equation 4.5) to the data

$$R = R_o * \exp(-E_A/K_B T) \dots\dots\dots 4.5$$

Where R is the resistance, R_o is the pre-factor, k_B is the Boltzmann constant 8.8173 x 10⁻⁵ eV/K and E_A is the defect activation energy

The slope of the curve Ln R vs T gives E_A. Good TAC fit is obtained in the temperature range 270 K to 400 K, as shown in Figure 4.13 (b). The defect activation energy is calculated to be 0.39 eV. Such low activation energy indicates degenerate semiconductor behavior where the fermi level almost resides in the energy bands. As temperature is decreased further, thermal activation doesn't dominate the conduction anymore. In the temperature range 65 K – 255 K Mott-VRH conduction is observed which can be represented by Equation 4.6

$$R = R_o * \exp\left(-\frac{T_M}{T}\right)^{\frac{1}{4}} \dots\dots\dots 4.6$$

where R is resistance, R_o is a weak temperature dependent pre-factor (value of R at T → ∞), T_M is the characteristic Mott temperature. Carrier hopping from one localized state to the other occurs through phonons, and that is why this is also called “phonon mediated hopping”. Electron distribution in the localized states present in the band gap is governed by Fermi-Dirac statistics. The density of states near the Fermi level is assumed to be constant (kT << E_F). Mott-VRH conduction mechanism occurring over a broad temperature range in this film suggests the existence of high density of defects in the material. High value of Mott temperature T_M (or T_o) of 3.9 x 10⁵ K also supports high defect density. Lowering the temperature further induces a crossover from Mott-VRH to ES-VRH transport at about 35 K in Figure 11 (c). ES-VRH conduction may be represented by Equation 4.7

$$R = R_o * \exp\left(-\frac{T_{ES}}{T}\right)^{\frac{1}{2}} \dots\dots\dots 4.7$$

Note that Equations 4.6 and 4.7 are similar except that the exponent changes from ¼ to ½ in the case of Equation 4.7. T_{ES} in Equation 4.8 represents a characteristic temperature. Contrary to the assumption of constant DOS at the fermi level in Mott's mechanism, a coulomb interaction is assumed in ES-VRH mechanism which opens a soft gap in the DOS. When the temperature is decreased, the coulomb interaction energy between carriers starts to dominate and opens a gap known as 'Coulomb gap' Δ that has a finite width. This phenomenon is an ensemble effect of a system of interacting electrons. As the thermal energy is increased, coulomb gap vanishes as $k_B T \gg \Delta$. T_{ES} is the quantitative measure of the disorder and localization lengths. The observation of this crossover to ES-VRH is evidence towards inhomogeneous conducting clusters in the film. After such a rigorous characterization of charge transport in the sample, it can be safely concluded that these complex transport mechanisms occurring in this material at the different temperature ranges are intrinsic to the material. To validate this model of conduction, theoretical crossover temperature can be computed using Equation 4.8

$$T_{cross} = 16 T_{ES}^2 / T_M \dots\dots\dots 4.8$$

which yields $T_{cross} \sim 50$ K for our pyrite which agrees well with the experimentally observed range in this study of the Mott-ES VRH crossover 35 K – 65 K.

In conclusion, it can be stated that high crystallinity and phase purity usually measured by XRD and Raman spectra do not warrant conduction homogeneity in the material. High degree of crystal disorder exists even in high phase purity films. We received ample experimental evidence to indicate the inhomogeneous conduction in the pyrite thin films with hopping transport at low to intermediate

temperatures and conventional band to band transport at high temperatures. Sulfur vacancy formation may cause such nanoscopic variations and account for observed high conductivity. This supports the hypothesis that stoichiometric variations are accommodated by local phase change and impact the electronic properties significantly. Higher conduction along with above discussed analysis explains the lack of photoresponse from the sample. In spite of this, such high conductivity films with d orbital transition metal chemistry makes it a promising candidate for catalysis purpose in solar cell device. High conductivity, scalable synthesis with material abundance makes it ideal for catalysis application in dye sensitized solar cell (DSSC). To access the applicability and performance of the pyrite films prepared in this study, DSSCs are presented in the next section using pyrite as counter electrode.

4.2.6 Devices

DSSCs hold great promise as a viable alternative to silicon based cells, especially for indoor applications. Research efforts have been dedicated to reduce the cost and to the scale up of technology to commercial level. DSSCs comprise of three major components namely, photoanode, photocathode and electrolyte. At the photoanode, electrons in dye molecules excited by the photons are transferred to a wideband gap semiconductor such as TiO₂ and ZnO.³² The redox couple in the electrolyte reduces the dye back to its ground state and in turn accepts the electron from the counter electrode catalyst which is usually platinum (Pt). I₃⁻/I⁻ based electrolyte is commonly used in DSSC. Since the photo voltage in DSSC depends on the redox potential of the electrolyte, the choice of electrolyte is vital. The highest efficiency DSSCs employ cobalt based electrolytes due to the higher difference in the Fermi level of the semiconductor (usually TiO₂) and the redox potential of the cobalt based electrolyte.³³ Pt or carbon is commonly used for counter electrode in DSSC due to their good catalytic activity. Pt gives good performance but it raises the cost of the cell. Carbon on the other hand is cheaper

but exhibits lower catalytic performance. Therefore, researchers have strived to develop alternative counter electrode materials which could possess the advantages of both Pt and carbon. Candidate alternative materials include transition metal oxides, sulfides, nitrides, carbides and also carbon and graphene. Notably, the choice of counter electrode material is different for different electrolytes. Pt performs best in I₃⁻/I⁻ redox couples, while PEDOT is the catalyst of choice for cobalt based electrolytes. It should be highlighted that latter one (PEDOT electrolyte) is more interesting as very few materials perform well with that electrolyte.

To reduce the overall resistance and low parasitic resistance, counter electrode material must possess high conductivity and exhibit high catalytic activity towards redox species of the electrolyte. High number of catalytic sites improves the kinetics of the reaction. To drive the redox reaction efficiently, following reaction must happen³⁴

And,

To examine the catalytic activity of pyrite cathodes, cyclic voltammetry (CV) was carried out in a three electrode system (working electrode, reference electrode and counter electrode). The electrolyte used was 10 mM LiI, 1 mM I₂ and 0.1 M LiClO₄ in acetonitrile solution. Scan rate was fixed to 100 mVs⁻¹. Positive current peaks correspond to the oxidation reaction while negative current peaks are the reduction reaction of I₃⁻/I⁻. Two pairs of oxidation and reduction peaks appear in CV scan, as shown in Figure 4.14 for both Pt and pyrite. Cathodic peaks signify the reduction potential at which the reactions occur.

Figure 4.14 CV scan of (a) as-sprayed FeS₂ film on FTO substrate, (b) as-sprayed and sulfurized FeS₂ film on FTO (blue) and Pt electrode (red).

Figure 4.14 (a) shows CV from an as-sprayed sample on FTO. Absence of redox peaks indicates no catalytic activity. While the positive oxidation current at high bias and negative reduction current due to high negative bias resembles close to bare FTO CV feature. Hence as-sprayed films were not catalytically active. Pyrite film formed after the sulfurization at 400° C for 30 mins shows reduction and oxidation peaks, as shown in Figure 4.14 (b). The CV curves of from pyrite film resembles closely to that of Pt indicating similar performance to catalyze the above reactions in the dye. Notably, the reduction peaks associated with I₂ to I₃⁻ and I₃⁻ to I⁻ reduction processes due to pyrite is slightly shifted to the right by approximately 0.05 V with respect to Pt peaks, signifying that the reaction occurs slightly easier for pyrite CE. Similar CV measurements are shown for the Co(III)/Co(II) redox electrolytes in Figure 4.15. Current densities obtained from CV plots show higher values for pyrite with Co(III)/Co(II) electrolyte in comparison to PEDOT as counter electrode indicating that pyrite can be an efficient counter electrode for this dye system too.

Figure 4.15 (a) CV scan of FeS_2 and PEDOT (both on FTO) with Co electrolyte, (b) Logarithmic plot of current density vs potential.

High number of catalytic sites is favorable to improve the kinetics of this system. Surface roughness plays an important role in this context as high surface roughness offers a greater effective area and, therefore, is desirable. Surface scans of the film done by AFM tapping mode are shown in Figure 4.16 (a), (b) and (c), the surface roughness of the pyrite films are found to be around 34.9 nm while for Pt and PEDOT, the surface roughness are around 2.5 nm and 0.8 nm respectively. The higher roughness, good catalytic activity as well as the high conductivity further supports the application of pyrite made in this project as a counter electrode.

Figure 4.16 Surface morphology of (a) Pt coated on FTO, (b) FeS_2 thin film on FTO and (c) PEDOT on FTO.

Finally, pyrite counter electrode DSSC devices were made with I₃⁻/I⁻ and Co(byp)₃³⁺/Co(byp)₃²⁺ electrolytes, and the resulting J-V characteristics and the external quantum efficiency (EQE) (which is similar to incident photon to current conversion efficiency IPCE) data shown in Figure 4.17. The data was measured under 1 Sun AM 1.5 illumination (100 mW/cm²).

Figure 4.17 (a) J-V curve and (b) IPCE of the FeS₂ and Pt counter electrode device with I₃⁻/I⁻ electrolyte. (c) J-V curve and (d) IPCE of the FeS₂ and PEDOT counter electrode with Co(III)/Co(II) electrolyte.

J-V curve for I₃⁻/I⁻ electrolyte shows efficiency of 7.97 % with pyrite counter electrode, which is higher than 7.54 % obtained for device with Pt counter electrode. Major contribution to the efficiency comes from the improvement in the current density. Current increases to about 2 % which is manifested by the enhanced EQE spectra. CV spectrum of pyrite was similar to that of Pt. This current density improvement was unexpected. The reasons for this are evident in the EQE spectra. Pyrite CE shows higher current from the photons with longer wavelengths, thus contributing to the higher efficiency. Higher wavelength

photons usually scatter more, which might have contributed to increased photon density within DSSC from pyrite surface. In the case of Co electrolyte DSSC, pyrite performs similar to PEDOT counter electrode. Superior current densities obtained in Co electrolyte DSSC is consistent with the CV measurement shown in Figure 4.15 showing high current density with pyrite. EQE also shows enhanced current throughout the spectrum. To evaluate the contribution from possible light reflection from pyrite CE surface, the effect of light intensity on performance was analyzed and the results are shown in Figure 4.18 (a).

Figure 4.18 (a) J-V characteristics of FeS_2 and Pt counter electrode DSSC cells at different light illumination intensities, (b) Reflectance spectra from Pt, FeS_2 and PEDOT films.

As the light intensity is reduced to 0.5 Sun and 0.1 Sun, Short circuit current (J_{sc}) becomes equivalent to that of Pt CE cell. At low intensities, light reflection from the pyrite surface becomes insignificant and hence, its advantage on the cell performance is lost. Comparison of reflectance from the pyrite surface with Pt and PEDOT clearly shows higher light reflection from pyrite. This supports the notion that the observed performance enhancement when using pyrite CE is used is from light reflection from the electrode surface.

To evaluate the electrochemical performance of pyrite counter electrode in DSSC, electrochemical impedance analysis was adopted to extract the key performance

parameters for a catalyst. Impedance spectroscopy is a widely used technique to characterize the charge transfer between semiconductors and electrolytes. Symmetric cells were prepared in order to evaluate the electrochemical properties of the counter electrodes. In symmetric cells, two features are observable in the recorded spectra: a low frequency feature which accounts for the electrolyte diffusion and a high frequency arc due to the charge transfer at the interface.³⁵ The measurement of symmetric cells in I_3^-/I^- electrolyte shows smaller high frequency arc for FeS_2 than Pt, in Figure 4.19 (a). A smaller high frequency arc is caused by a lower charge transfer resistance from electrolyte to counter electrode. This confirms the higher catalytic activity of FeS_2 counter electrode compared to Pt, which is also reflected in the overall performance of the DSSC device. This is not reflected in the final fill factor (FF) of the DSSC devices, probably due to the higher electrical conductivity of Pt which compensates for its lower catalytic effect, and hence results in a similar total series resistance.

Figure 4.19 Electrochemical impedance spectra (EIS) of (a) FeS_2 and Pt electrode with iodide electrolyte and (b) FeS_2 and PEDOT electrode with cobalt electrolyte.

Table 4.2 Photovoltaic cell parameters from pyrite CE and PEDOT CE devices along with the fitted parameters extracted from impedance spectroscopy of the symmetric cells

Counter electrode	$R_s^{a)}$ [$\Omega\text{-cm}^2$]	$R_{ct}^{b)}$ [$\Omega\text{-cm}^2$]	C [μF] ^{c)}	Total $R^{d)}$ [$\Omega\text{-cm}^2$]
FeS₂	4.9	7.2	92	12.1
PEDOT	6.0	3.9	2.3	9.6

The symmetric cell responses in Co(III)/Co(II) electrolyte with FeS₂ and PEDOT electrodes showed different response, as shown in Figure 4.19 (b). Parameters extracted from fitting the impedance data with the model are listed in Table 4.2. Total resistance R which is the sum of the series resistance and charge transfer resistance, is calculated to be $12.1 \Omega\text{-cm}^2$. This value is comparable to the value of $9.6 \Omega\text{-cm}^2$ obtained for PEDOT. Impedance spectroscopy shows a higher charge transfer resistance for the FeS₂ sample, Figure 4.19 (b) and consequently, a lower FF was observed for FeS₂ CE. However, double layer capacitance value calculated for pyrite found to be $92 \mu\text{F}$ while for PEDOT $2.3 \mu\text{F}$. Higher double layer capacitance value reflects an effectively higher effective surface area of pyrite films resulting from its higher roughness of 34.9 nm compared to 0.8 nm for PEDOT demonstrated by AFM. This effective surface area increment of pyrite film compensates for the lower charge transfer resistance and results in overall comparable conversion efficiency with PEDOT. This is confirmed by impedance measurement for the symmetric cell configuration.

4.3 Conclusions

- Post sulfurization treatment of the as-sprayed films is necessary to convert the amorphous films to crystalline, single phase, pyrite films.
- Sulfurization conditions are required to achieve the pure pyrite phase are heat treatment in the temperature range of 400° C – 500° C for 30 mins.
- The Fe:S ratio close to the stoichiometric value of 1:2 is obtained after sulfurization but the surface is prone to defects such as formation of monosulfide species.
- Bandgap value measured from optical absorption Tauc analysis is about 1.04 eV. This value fits with a direct band gap relation, possibly indicating the presence of defects in the film.
- Sulfurized films show p-type conductivity from Hall and Seebeck measurements with high hole concentration and degenerate semiconductor behavior.
- Sprayed and sulfurized films show no photoresponse.
- Electrical conduction in these films occur via the Mott-variable range hopping conduction mechanism as proven by the temperature dependent electrical transport measurements. Crossover to ES-VRH conduction mechanism occurs at temperatures less than 35 K.
- Hopping conduction crossover demonstrates the presence of localized gap states in the pyrite. Localization lengths calculated from the measurements is < 1 nm. Electronic disorder in the material causes non-homogeneous conduction in the film and the gap states are responsible for high conductivity degenerate behavior.
- Sprayed and sulfurized pyrite films showed high catalytic activity in reducing the redox couple I₃⁻/I⁻ and Co(III)/Co(II) electrolyte.
- Dye Sensitized Solar Cells (DSSC) made form FeS₂ counter electrode with I₃⁻/I⁻ and Co(III)/Co(II) redox electrolyte showed good performance. The solar cell sing pyrite counter electrode performed equally well to the

state of the art electrodes Pt and PEDOT for I₃⁻/I⁻ and Co(III)/Co(II) redox electrolyte respectively.

- Low charge transfer resistance, high surface roughness and better light reflection from the electrode surface contributed to the good performance of pyrite counter electrode in a DSSC.

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Chapter 5

Study of Iron Pyrite (FeS₂) Nanocubes and Their Spin-Coated Films

With the recent advances in nanotechnology and colloidal chemistry, nano crystal synthesis has become relatively easy. Even precise control of particle size and shape has become possible with the use of surfactants.¹ Nanocrystals made by such controlled chemistry could have unique properties if the crystals could be made to have crystallographic facets with special surface properties.^{2,3} Nanocrystals made from semiconducting materials are being studied for various optoelectronic applications. We intend to exploit such nanotechnology expertise to synthesize high quality pyrite nanocrystals, in order to shed light on the basic photophysics and charge transport mechanisms and unravel the peculiar behavior reported in pyrite. Adaptation of a suitable synthesis conditions developed by a co-researcher could yield (100) faceted, cubic iron pyrite single crystal nanocubes. (Hu Ge PhD Thesis, 2016) on which the characterizations were performed.

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5.1 Synthesis and Film Fabrication Procedures

5.1.1 Synthesis of Pyrite Nanocubes

Solution processed hot-injection method was used to prepare controlled (100) faceted pyrite nanocubes. Synthesis approach was adopted from the doctoral work by Hu Ge, where he investigated synthesis conditions to produce pyrite nano particles of different morphologies by solvent engineering and by studying the impact of temperature and precursor concentrations. These are discussed in detail by Hu Ge in his doctoral thesis. In this work, we choose pyrite nanocubes for detail investigations of their optoelectronic properties. Synthesis procedure followed is described below.

The starting materials for the synthesis were 98% anhydrous Iron (II) chloride (FeCl₂), 70 % oleylamine (OLA), and sulfur powder from Sigma-Aldrich. 0.5 mmol (63.5 mg) of FeCl₂ was mixed with 5 mL OLA in a tri-neck flask and degassed for 30 minutes. Subsequently it was heated to 110° C for 1 hour to form the Fe-OLA complex. Thereafter, the temperature was raised to 180° C and 3 mmol (96 mg) of sulfur dissolved in OLA was injected into the flask. The temperature was maintained at 180° C for 24 hours to complete the reaction. After reaction, the solution was allowed to cool to room temperature naturally and a large amount of methanol was added to precipitate the FeS₂ nanocubes. The product was concentrated by centrifugation and then dispersed in hexane. 50 µL of Pyrite NCs suspension with a concentration of (0.1M) was spin-coated on a glass substrate sequentially to obtain a pyrite film which was used to carry out characterizations.

5.1.2 Post Heat Treatment

Nanocubes spin coated on the substrate were annealed in sulfur ambient at 500°C for 30 mins similar to the post sulfurization treatment given to spray pyrolyzed films discussed in Chapter 4 but some details were different. Sulfurization treatment was carried out in a two-zone furnace. The sulfur powder was kept at 200°C at one zone and the sample was maintained at 500°C in the other zone of a two zone quartz tube furnace. Chamber was pumped down and evacuated 3 times and backfilled with Ar gas to make sure an oxygen-free and moisture-free environment for the treatment. Ar gas fed into the chamber to get a constant pressure of 300 mbar inside the tube and then the temperature was ramped up for sulfurization. The schematic of the process is shown in Figure 5.1.

Figure 5.1 Schematic of the sulfurization set up.

The purpose of this heat treatment was to remove the insulating ligands, achieve good conductivity and good interparticle contact to enable better charge transfer while, most importantly, maintaining the crystalline quality and phase purity of the nanocubes. After sulfurization treatment, nanocubes retain their shape.

5.2 Results and Discussions

5.2.1 Characterization of As-prepared Nanocubes

Figure 5.2 shows XRD and Raman spectra of the as prepared pyrite nanocube film. Intense XRD peaks can be observed in the scan can be indexed to cubic phase of FeS₂ (JCPDS 00-042-1340).

Figure 5.2 (a) XRD pattern and (b) Raman spectra, of as-prepared FeS₂ nanocubes spin coated on glass substrate.

No phase impurities such as marcasite (orthorhombic) or FeS are detected in XRD. Lattice constants calculated from the peaks yield a value of $a = 5.392 \text{ \AA}$. As is usually done, we used Raman spectroscopy to augment XRD findings and confirm phase purity of the films as impurities may be present below the detection limit of powder XRD which is about 2 vol %. Figure 5.2 (b) shows the Raman spectra of the as-prepared spin coated nanocube film. Three modes at 341 cm^{-1} , 376 cm^{-1} and 424 cm^{-1} are observed corresponding to A_g, E_g and T_g(3) mode respectively, as shown in Figure 5.2 (b).⁴ Raman is very sensitive to the phase impurities. No other impurity peak is observed in the Raman spectra. Raman spectra shown in the Figure 5.2 (b) was recorded using micro-Raman set up with 532 nm laser wavelength. Laser illumination intensity seems to affect the spectra as shown in Figure 5.3. High illumination intensity most of the times showed Raman peaks corresponding to oxidation of the sample, showed as asterisk in Figure 5.3 To avoid laser irradiation induced oxidation, laser intensities below

0.5 mW were used for measurements.

Figure 5.3 Raman spectra of pyrite (FeS_2) nanocube film at different laser illumination powers.

The size of nanocubes was found to be fairly uniform and was around 100 nm on average. The film morphology could be seen in the field emission scanning electron microscope (FE-SEM) image shown in Figure 5.4 (a).

Figure 5.4 (a) Top-view SEM image of pyrite nanocubes. (b) TEM image of individual nanocube edge, lattice fringes and crystal planes are marked in orange. (c) TEM image of nanocube and inset shows selected area diffraction (SAED) pattern.

The nanocube morphology is evident in the film. Nanocubes exhibited a tendency to get charged under electron beam illumination in the SEM after a while which indicates a poor electrical conductivity across the cubes. This is due to the insulating organic ligands attached to the surface of the nanocubes which are derived from the synthesis procedure. High resolution transmission electron microscopy focused at the edge of the nanocube shows clear lattice fringes and the corresponding crystal directions are marked in Figure 5.4 (b) which indicate that the cube facets are (100) planes. Selected area electron diffraction (SAED) also shows clear diffraction spots that could be indexed to (200) and (020) planes which further confirm the presence of (100) facets on the cube, as shown in Figure 5.4 (c). Besides, it is clear that the cube is a single crystal from the SAED pattern and lattice fringes. Lattice constant calculated from the SAED pattern corresponds well with that obtained from XRD. These observations confirm that we have successfully synthesized pure pyrite single crystal nanocubes with (100) facets.

5.2.2 Optical Properties

Optical absorption measurements were conducted on the films obtained by spin coating the nanocubes on glass substrate. High optical absorption above the band edge was observed as expected. Significant absorption below the band gap was observed. Careful interpretation of the band edge and the value of the band gap are required. The inconsistency in the literature regarding the band gap of pyrite is commonly known.

Figure 5.5 (a) Optical absorption (Absorbance vs wavelength) spectra of as-coated pyrite nanocube film, (b) Ln A vs Energy and (c) Tauc plot analysis of as-prepared spincoated iron pyrite nanocubes thin film, intercept at 0.85 eV corresponding to direct band gap.

Sub-band gap absorption obscures the “actual” band edge leading to erroneous estimates of the band gap from experiments and even the direct and indirect nature of the transition is debatable.⁵ Like spray pyrolyzed thin films discussed in Chapter 4, these nanocube films also fit with the direct optical transition exponent ($n = 2$), depicted in Figure 5.5 (c). The direct band gap energy comes out to be ~ 0.85 eV for as-spin coated nanocube films.

Electrical measurements made on these samples yield very low currents due to the insulating ligands attached to the cube facets. Hall measurement showed the sample to be p-type with very low hall coefficient and low current values. These films were certainly not suitable to make devices or to perform detailed electrical characterizations. Therefore, a post annealing treatment was specially developed to enhance the electrical performance of spin coated nanocube films.

5.2.3 Structural Characterization of Heat Treated Films

XRD pattern and Raman spectra of the film is shown in Figure 5.6. All the XRD peaks can be indexed to the cubic pyrite phase, as shown in Figure 5.6 (a). Lattice parameter measured from XRD (similar to as-prepared films) comes out as $a = 5.412$ Å, very close to the value reported by Birkholz *et al.* on high quality single

crystals.⁶ Birkholz *et al.* claimed that XRD lattice parameter change is directly related to the sulfur deficiency in the sample. The value close to their lattice parameter value indicates equivalent crystalline quality of nanocubes to the high purity single crystals prepared by chemical vapor transport (CVT). Raman spectroscopy for sulfurized films show similar Raman spectra as pure pyrite phase suggesting that sulfurization treatment does not instigate other phase formation, as shown in Figure 5.6 (b). No phase impurities such as FeS, Fe₃S₄, Fe_{1-x}S and marcasite are observed both in XRD and Raman investigations.

More detailed specifications of crystal quality come from HRTEM analysis. Individual nanocube is examined in a TEM. Notably, the charging effect observed in samples before heat treatment, was not observed in these films. Figure 5.7 shows the high resolution TEM, lattice fringes and SAED pattern of the nanocube.

Figure 5.6 (a) XRD pattern and (b) Raman spectra of sulfurized pyrite nanocube film.

Figure 5.7 HRTEM image of the sulfurized iron pyrite nanocubes (a) Full nanocube and edge of the nanocube, (b) lattices fringes and stacking faults marked by yellow dashed lines and arrows, (c) selected area electron diffraction (SAED) pattern indicating the points corresponding to marked planes.

Single crystallinity of the sulfurized nanocubes is evident in the HRTEM images in Figure 5.7. The lattice resolved high resolution image yields a lattice constant of 5.48 Å, in congruence with the (100) plane lattice spacing shown in Figure 5.7 (c). SAED pattern shows two pairs of planes which could be indexed to (200) & (2 $\bar{0}$ 0) and (020) & (02 $\bar{0}$) as shown in Figure 5.7 (c). The zone axis of the cube is [001] which proves that they are terminated with (100) facets. Planar defects such as stacking faults could be discerned in the lattice as marked with yellow lines and arrows in Figure 5.7 (b). Although, such defects have been previously reported in nanoparticles, their presence may have an important role in governing the opto-electronic properties of pyrite nanoparticles.^{7,8} Figure 5.8 shows the SEM of the nanocubes after the post sulfurization treatment.

Figure 5.8 Top-view SEM image of the pyrite nanocubes after the heat treatment process (500° C for 30 mins).

This proves the successful deployment of a heat treatment to remove the organic ligands while maintaining the shape of the nanocubes. This may be used for other chalcogenide nanoparticles as well. However, it still remains to prove that the relevant properties of the film are not affected.

The heat treated films were structurally very pure and high quality to be studied further. The heat treatment step involves two parameters, temperature and time. The temperature window was chosen intuitively from 300° C – 500° C due to thermodynamic considerations and from the previous experience with the spray

pyrolized films. 500° C proved to be most effective for pursuing the treatment for shorter dwelling time of 30 mins. On the other hand, heat treatment time seem to affect the crystal orientation but very sluggishly. Increasing the time enhances the (100) peak intensity, in particular. A similar phenomenon has been observed where annealing helps in preferential alignment of the nanocubes.^{9,10} Pole figure tests were carried out to examine the effect of heat treatment on the crystallographic orientation of the spin coated nanocube film. Pole figure measurements in Figure 5.9 give information about the preferential alignment of the crystals. Stereographic projection of the XRD diffraction gives intensity map corresponding to the different crystal orientations. Figure 5.9 shows the pole figure plot for the nanocube film heat treated for different times.

Figure 5.9 Pole figure plots of plane (002) (021) and (112) for the pyrite nanocube film as-prepared and heat treated for 3 hrs and 6 hrs at 500° C.

The main purpose of the heat treatment was to increase the electrical conductivity and improve charge carrier transport. Conductivity of the sample increased significantly after the heat treatment. Figure 5.10 shows the current-voltage curve of the nanocube film before and after heat treatment.

Figure 5.10 Current voltage characteristics of (a) As-prepared (central) and (b) heat treated iron pyrite nanocube thin films.

Current increased from nA range to mA range after heat treatment. This was consistently observed for all the samples. The I-V measurements were performed in-planar source-drain configuration. Aluminium (work function 4.2 eV) was used as a metal contact to make ohmic contacts. Hall measurement conducted in the Van der Pauw geometry showed p-type response. Detailed Hall parameters are listed in Table 5.1

Table 5.1 Hall parameters for heat treated film

Parameter	Value
Resistivity (Ohm*cm)	11.20
Mobility (cm ² /V-s)	0.10
Carrier density (cm ⁻³)	5.30 x 10 ¹⁸
Hall Coefficient (cm ³ /Coul)	1.17
Carrier type	Holes

5.2.4 Optical Absorption and Assessment of the Band Gap

Optical absorption of pyrite nanocubes were measured by UV-Vis absorption spectrophotometer. Optical absorption coefficient $\alpha > 1 \times 10^5 \text{ cm}^{-1}$ for $h\nu > 1.3 \text{ eV}$ obtained. Optical band gap of the material is calculated by Tauc plot analysis. From Figure 5.11, regions of different slopes can be identified from Tauc plot, which correspond to the optical excitation from band edges and also from defect states/bands. Linear extrapolations of the slopes give intercept on the energy axis that corresponds to the optical transition at that particular energy level. Electronic behavior of pyrite is governed by these energy level transitions. Three distinct energy transitions could be identified at 1.1 eV, 1.5 eV and 1.9 eV. From the analysis of Tauc plot, band gap is estimated at 1.1 eV, within the range (0.80 eV to 1.10 eV) of commonly accepted band gap value of pyrite.¹¹ However, this band gap value appears to be direct as it fits linearly with $n = 2$ value in the Tauc equation $(\alpha h\nu)^n$. Such unexpected indirect to direct transition is not unusual for semiconductors with high density of defect states and disorder and also reported for iron pyrite single crystals.¹² Similar is observed in the case of spray deposited thin films. Optical transition at 1.5 eV corresponds to the fundamental direct band to band excitation, consistent with previously reported values.¹³ Third transition at 1.9 eV agrees well with values approximated by theoretical study by Vadhiyia *et al.* and experimentation, attributed to the interband excitonic transition. Notably, the discrepancies commonly reported in the determination of optical band gap indicate fuzzy band edges of pyrite, a quintessential feature of disordered semiconductor.¹⁴ Potential fluctuations arising from defects perturb the electronic band edges, resulting in a broadening of electronic states forming band tails extending below the band edges giving sub-band gap optical absorption.^{15,16} From Figure 5.11 (b), absorption spectra can be divided in four parts, region I is due to optical transition from extended states to mid-gap localized states, region II is exponential tail due to transitions from one of the extended state to the other band tail localized states at absorption edge, region III

is due to power law dependence of absorption coefficient on photon energy and region IV is due to fundamental optical absorption. For iron pyrite, such defects may be intrinsic, i.e. sulfur and iron deficiency predicted by first principle studies.¹⁷ Absorption below the band gap indicates a feature known as Urbach tail, which is also used to explain the degree of disorder for semiconducting material.¹⁸ From Figure 5.11 (b), slope of the absorption below the band gap value is slightly higher for heat treated film than as-coated one, indicating that heat treatment helps in defect passivation likely by removing surface ligands.

Figure 5.11 (a) UV-Vis Optical absorption spectra, (b) Absorbance vs Energy, different regions correspond to specific optical excitations and (c) Tauc plot analysis of sulfurized pyrite film, indirect and direct band edge intercept at 0.72 and 1.02 eV, respectively.

5.2.5 Photoresponsivity

Heat treated iron pyrite nanocubes thin films were tested for photoresponse by depositing electrodes in a parallel source drain type configuration and the channel is irradiated with light as schematically shown in Figure 5.12.

Figure 5.12 Schematic of the photoresponse measurement configuration.

Upon irradiation, photocurrent increases sluggishly as a function of time. When the light is turned off, current very slowly relaxes to the original dark current values with a long decay time, as shown in Figure 5.13 (a). Figure 5.13 (b) shows transient response of photocurrent from the heat treated films. Fitting the photocurrent rise and decay with single exponential function yields long rise and decay lifetimes of 290 sec and 252 secs respectively. Such longer rise and decay times indicate slow generation and recombination process is associated with the trap states present within the band gap. Since this response is observed after heat treatment, the effectiveness of the heat treatment in this study and the previous studies is doubtful in improving the midgap defect driven relaxation processes.

Figure 5.13 (a) Transient Photocurrent response of heat treated pyrite nanocube film and (b) rise and decay lifetimes fitting by exponential function.

This is a qualitative proof of the deleterious effect of the gap states on charge carrier dynamics. This might be the major reason behind the poor pyrite performance in solar cells.

5.2.6 Probing the Charge Carrier Decay: Transient Absorption Spectroscopy

Transient absorption (TA) spectroscopy allows us to monitor the photo-generated charge carrier dynamics in as-spin coated and heat treated pyrite samples. The broad band dynamical TA spectra in the femtosecond and microsecond probe time delay ranges were measured with a HELIOSTM and EOSTM from ultrafast systems. Following photoexcitation with above bandgap 650 nm pump pulses, the hot charge carriers rapidly relax to the band edge and trap states. Figure 5.14 (a) & (c) show the pseudo color plots of the change in absorption (ΔA represented by the color scale) against wavelength (nm) and probe time delay (ps and μs) for the sulfurized sample. Similar TA spectra and dynamics for the as-spin coated and heat treated samples suggest that the intrinsic electronic property (crystallization) of pyrite is not changed much by the heat treatment (see Figure 5.15). This result further confirms that the dominant effect of this heat treatment is to remove the attached insulating ligands for better interparticle contact. Figure 5.14 (a) also shows a prominent negative ΔA band or photobleaching (PB) signature near the bandgap at around 950 nm. This PB band shows a fast decay with a lifetime (fitted with Equation 3.16 of Chapter 3) of 1.8 ps. This lifetime closely matches with the building up time of a broad positive ΔA band or photoinduced absorption (PIA) signature at wavelengths > 1000 nm. The band edge PB signal should originate from stimulated emission near the bandgap of the photo-generated carriers and state-filling of the band edge states; the broad PIA band below the band gap should originate from the localized charge carrier absorption. Therefore, the band edge PB fast decay represents photo-generated charge carrier localization from the direct gap edge to indirect band edge and mid gap trap states. Since, the sample is of p-type (measured using Hall analysis), fast

charge carrier localization most likely originates from the photo-generated electron localization and trapping. The recombination time of the trapped electrons with holes is of the order of few hundreds of ns (see Figure 5.14 (d)). Importantly, it is difficult to distinguish bulk and surface recombination components because transient absorption measured is from the whole sample.

Figure 5.14 Differential transient absorption spectra after photoexcitation of sulfurized iron pyrite nanocubes as a function of time delay in (a) femto-pico second range, (c) nano-micro second range. Carrier decay dynamics probed at 950 nm (photobleaching) and 1400 nm (photoinduced absorption) by fitting the transients in (b) picosecond range, fitted with single exponential decay function (solid black line) with decay time constant (charge transfer time, τ_{CT}) 1.8 ps and (d) microsecond range, fitted with biexponential decay function with time constants 50 ns (τ_{d1}) and 990 ns (τ_{d2}) associated with the long lived trap states and the eventual recombination process.

Figure 5.15 Differential transient absorption spectra after photoexcitation of as-prepared iron pyrite nanocubes as a function of time delay in (a) femto-pico second range, (c) nano-micro second range. Carrier decay dynamics probed at 950 nm (photobleaching) and 1400 nm (photoinduced absorption) by fitting the transients in (b) picosecond range, fitted with single exponential decay function (solid black line) with decay time constant (charge transfer time, τ_{ct}) 1.8 ps and (d) microsecond range, fitted with biexponential decay function with time constants 50 ns (τ_{d1}) and 990 ns (τ_{d2}) associated with long live trap states and eventual recombination process.

Based on the above analysis, schematic of the carrier relaxation can be drawn. The schematic is shown in Figure 5.16.

Figure 5.16 Representative schematic of the photophysical processes involved in iron pyrite based on optical pump probe spectroscopy. (1) optical excitation of electron from valence to conduction band, (2) rapid carrier localization of the excited carrier to indirect band edge and low lying shallow defect states, (3) slower electron relaxation to mid-gap deep defect states/band (long lived trap states) and (4) electron recombination process with the valence band holes.

So the excited carriers relax very fast to the band edges that are connected through shallow defect levels. Connected density of states enables rapid carrier relaxation to localized states. This quick relaxation makes it extremely difficult to extract the carriers out and generate a high photovoltage commensurate with the full band gap. Instead the carriers that are relaxed quickly to deeper lying mid gap states extracted yielding a lower photovoltage.

5.2.7 Electrical Transport

A high density of defect states indicated by previous investigations discussed in this chapter will have a significant impact on the charge transport properties of the film. Electrical conduction by charge carriers is affected by scattering due to defects. The operating scattering mechanism changes with temperature giving different temperature regimes where each mechanism dominates. Figure 5.17 shows the electrical transport measurements from heat treated pyrite nanocube films.

Figure 5.17 (b) shows the dependence of resistivity ($\ln \rho$) on $1/T$. The $dR/dT < 0$ relation of the film is typical semiconducting behavior. When the results are plotted against $T^{-1/4}$, a good straight line could be fitted by Equation 5.1 with $d = 3$, from room temperature (300 K) to about 50 K as shown in Figure 5.17 (b). This indicates a good agreement with Mott variable range hopping (VRH) mechanism for charge transport given by the equation

$$\rho = \rho_0 \exp (T_0/T)^{1/d+1} \dots\dots\dots 5.1$$

where d in the exponent is the dimensionality of the system, T_0 is the characteristic temperature and ρ_0 is a weak temperature dependent pre-exponential factor (value of ρ at $T \rightarrow \infty$) which depends on the electron-phonon interactions.¹⁹ It is to be highlighted that the density of states (DOS) is assumed to be non-zero and constant at the Fermi level within the thermal energy interval between localized states in the equation. A high characteristic temperature of $T_0 = 4.5 \times 10^6$ K was obtained by linear curve fitting of $\ln(\rho)$ vs $T^{(-1/4)}$. Such conducting behavior is marked by charge transport through the localized states via phonons (phonon assisted transport). At finite temperature, VRH conduction is caused by the localized states that depend on dimensionality (d) of the system.²⁰ Since the charge transport in our films is through nanocubes, the value of $d = 3$

could be used due to 3- dimensional isotropy of nanocubes. Moreover, deviation from $d = 3$ is not anticipated as the characteristic length scales are too small for iron pyrite to observe such transitions or crossover in these nanocubes. This argument agrees well with the experimental data fitted with 3- dimensional VRH Equation 5.1. This is similar to the behavior observed for spray pyrolyzed thin films discussed in Chapter 4. Also, previous transport studies on iron pyrite single crystals and nanostructures showed Mott-VRH type conduction phenomena.²¹ The fact that Mott-VRH type conduction behavior is often observed in different pyrite nanostructures, regardless of the synthesis procedures used, reinforces the existence of smaller localization lengths and intrinsic defect mechanisms in iron pyrite. Disorder and intrinsic defects cause localized states (Anderson localization) within the band gap and electron hops from one site to another spatially separated site.²² The selection of the site is based on the criteria of minimum activation energy (minimum energy difference) configuration that maximizes the hopping probability. However, the temperature dependence of resistance below 50 K is quite complicated. Responsible factors can be metallic conductivity onset or fluctuation induced tunneling (FIT) across the nanocubes.²³ Tunneling possibility exists, as the nanocubes are physically in contact and some barrier may form at the interface due to the difference between the bulk and the surface conductivity. A detailed focused investigation of pyrite transport at low temperatures less than 50 K is necessary but is outside the scope of this project.

Figure 5.17 (a) Temperature dependent resistance (R-T) of heat treated nanocubes thin film, (b) activated transport $\ln \rho$ vs $1/T$ and (c) Mott-VRH transport $\ln \rho$ vs $T^{-1/4}$ plot.

It is clear from the resistivity dependence on temperature that the presence of high density of defect states proven by transient absorption optical pump-probe studies discussed in Section 5.2.6 has a deleterious effect in the photovoltage achievable from pyrite driven solar devices. Besides, the Mott-VRH transport mechanism observed over most of the temperature range is in full agreement with the photo physical charge relaxation behavior proposed in Figure 5.16. Improvement of the pyrite performance as a photon absorber in solar devices depends critically on eliminating or controlling these defect states. It is therefore vital to understand the origin of these defect states since the synthesized pyrite nanocubes was found to be free of impurity phases or elements.

5.2.8 Magnetic Measurements

FeS₂ is a non-magnetic (diamagnetic) semiconductor while other possible iron sulfide phase in the Fe-S binary system exhibit different magnetic ordering at room temperature. For example, FeS is antiferromagnetic, Fe_{1-x}S is ferromagnetic, Fe₇S₈ is ferrimagnetic and elemental Fe is a long range ferromagnet.²⁴ Significant magnetic ordering of other phases makes it easier to identify impurity phases by sensitive magnetic measurements. Theoretical studies in the literature have shown that stoichiometric or sulfur deficient (100)

surfaces of pyrite crystals will have a net magnetic moment.^{25,26} Sulfur vacancies at the surface could be readily accommodated by monosulfide species.²⁷ Altered local Fe coordination due to sulfur vacancy also energetically causes bonding and antibonding states to shift/split, producing gap states.²⁸

Temperature dependent magnetization data was obtained from room temperature down to 10 K using SQUID magnetometer. The data is shown in Figure 5.18 (a). It can be clearly seen that below about 50 K, some magnetic ordering is evident leading a significant increase in magnetic moment. This might occur if the magnetic ordering energy becomes more than the thermal vibration energy. Isothermal M-H measurements conducted at 300 K and 10 K are shown in Figure 5.18 (b). Typical diamagnetic behavior is observed at 300 K but, at 10 K a weak magnetic ordering is exhibited giving a measurable saturation magnetic moment. This raises the possibility of the formation of magnetic impurity phases, such as FeS_{2- δ} ($0 \leq \delta \leq 1$), at low temperatures which could be the consequence of non-stoichiometry at localized regions caused by clustering of sulfur vacancies within the bulk, or near the surface. Such possibilities have been raised in a number of studies.^{24,29} Since, such phases were clearly not detected at room temperature; this phenomenon of magnetization at low temperatures could be attributed to the point defects clustering at low temperatures which might create nano-scale regions of non-stoichiometry and consequently local magnetic ordering.³⁰ At low temperatures, another possible mechanism for detecting magnetic moment may be due to the freezing of defect spins which enable magnetic exchange to occur versus thermal fluctuations which tend to destroy the alignment and hence magnetism.

Figure 5.18 Magnetic measurements of iron pyrite nanocube film. (a) Magnetization vs temperature plot from 300 K to 10 K and (b) M-H curve at 10 K and 300 K temperature showing superparamagnetic and diamagnetic response, respectively.

The origin of magnetic moment can be explained combining the two effects discussed previously, in terms of geometrical consideration of the Fe-S coordination in the pyrite crystal. LFT and MO theories predict the formation of midgap defect states/band due to sulfur vacancies. The Fe atom in iron pyrite is in octahedral coordination (Fe-S₆) with S. Due to strong ligand field (S atoms), Fe d-states split and form valence and conduction bands which are derived from t_{2g} and e_g states respectively. Electrons in these states are distributed in low spin configuration and hence pyrite is non-magnetic at room temperature. When S vacancies are created, the local coordination of Fe (such as FeS₅, FeS₄...etc.) is reduced which leads to symmetry reduction. This causes further splitting of Fe d-states and introduces additional states in the forbidden energy gap. Electron distribution is no longer in low spin configuration (fully filled orbitals) giving rise to some high spin configurations due to splitting of t_{2g} state, resulting in localized magnetic spins.²⁸ At low temperatures when the thermal vibrations are low, the crystals tend to reduce its total energy by S vacancy diffusion into some low energy configurations where exchange coupling of the unpaired electrons could occur through the Fe ions. This could lead to ferromagnetism in localized regions of the crystal where it becomes detectable by a sensitive magnetometer. Since point defects are a source of localized gap states, the magnetic information is also consistent with the photophysical process discussed in Sections 5.2.6 and

5.2.7. The characteristics of defects depend mostly on the growth conditions. These magnetic property results demonstrate the effectiveness of magnetic measurements as a complimentary technique in studying a complex point defect system along with the other techniques employed in this project.

Thus, on the basis of optical, electrical and magnetic studies, the complete comprehensive picture can be now presented schematically as in Figure 5.19.

Figure 5.19 Schematic of the density of states, photocarrier loss processes and electrical conduction mechanism derived from optical, electrical and magnetic measurements.

5.2.9 Heterojunction Solar Cell

The heat treated nanocube iron pyrite films were evaluated for solar absorption performance in a heterojunction solar cell. A junction was made between the p-type pyrite film and n-type wide band gap CdS. CdS was chosen due to its

favorable band energetics with pyrite for efficient extraction of charge carriers. Figure 5.20 shows the current density versus voltage (J-V) curve of the solar cell under 1 Sun (100 mW/cm²) illumination. A photovoltage of around 94 mV was obtained with FF of 0.28 and current density of 0.4 mA/cm² showing that the heat treated iron pyrite nanocube film could be used as solar absorber material. Figure 5.20 (b) shows the external quantum efficiency (EQE) of the FeS₂-CdS heterojunction solar cell, shows photocarrier collection band edge close to the band gap of pyrite.

Figure 5.20 (a) Current density vs voltage (J-V) curve of iron pyrite heterojunction solar cell, (b) external quantum efficiency of the heterojunction solar cell, (c) schematics of energy band alignment of different layers of the solar cell and (d) cross-section SEM of the measured solar cell.

Figure 5.20 (c) shows the schematic of charge transfer process in a pyrite nanocube/CdS heterojunction device. Energy band position of CdS and FeS₂ nanocubes are favorable for charge carriers to be extracted by the hole and electron selective contacts. Cross-section SEM image of the device is shown in Figure 5.20 (d). Active layer, top and bottom electron and hole collecting layers

are distinct and can be clearly seen in the Figure 5.20 (d). The low photovoltage obtained is consistent with the charge carrier dynamics of pyrite elucidated previously in Sections 5.2.6 to 5.2.8. Femtosecond transient photocurrent spectroscopy showed photocurrent generation at different wavelength. Photocurrent spectra consistently followed optical absorption, demonstrating that the excited carriers are converted to electrical current, as shown in Figure 5.21 (a). Also, fitting of transient photocurrent spectra with the single exponential decay function yields carrier lifetimes of the order of $\sim \mu\text{s}$ could be obtained as indicated in Figure 5.21 (b). This proves that the extracted photo current is not from the conduction band electrons but from electrons relaxed to deep defect trap states where their transient dwell time is larger than in the shallow defect states.

Figure 5.21 (a) Photocurrent measured from femtosecond transient photocurrent spectroscopy (right) and absorption spectra (left) and (b) Transient photocurrent decay at various wavelengths under 100 mW/cm² illumination power.

5.2.10 p- FeS_2 -n Photodiode

A photodiode was fabricated from pyrite nanostructures as solution based synthesis allows us to deposit films on various platforms. To harness the photocurrent generated in pyrite, perhaps the best architecture of a diode would be a p- FeS_2 -n configuration. Electron and hole selective interfaces provide better driving force to the carrier to be swept away across the interface. Electric field generated due to the difference in energy band enables field assisted carrier separation. The device geometry and configuration used is shown in Figure 5.22 (a) and cross section SEM in Figure 5.22 (b). Schematic of the devices shows FeS_2 sandwiched between Copper iodide (CuI) p-type and Zinc oxide (ZnO) n-type. Cross-section image of the device from SEM shows distinct layers of the individual constituents. Light was irradiated from the p side. This type of configuration is also called “Inverted architecture”.

Figure 5.22 (a) Schematic of the photodiode, (b) cross-section SEM of the photodiode showing individual layers of the device.

Figure 5.23 (a) Current-Voltage (J-V) characteristics of CuI/FeS₂/ZnO photodiode under dark and AM 1.5 light illumination, inset shows J-V curve with current plotted in semi-logarithmic scale. (b) Transient response of the photocurrent under zero bias voltage.

The J-V curve of this device shows a typical diode characteristics as in Figure 5.23 (a). Photocurrent enhancement can be clearly seen under illumination. Rectification ratio at ± 1 V is around 197. Short circuit current density of $J_{sc} \sim 0.5 \text{ mA/cm}^2$ is obtained with a very small photovoltage (V_{oc}) of about 5 mV. This indicates the possibility of self-powered operation of the device. Transient response from the device shows recovery times of < 1 sec with on-off ratio of 371. Figure 5.24 shows the internal photon to current conversion efficiency (IPCE) and responsivity at different wavelengths. Responsivity is calculated from the Equation 5.2.

$$R = \text{IPCE} * \lambda / 1240 \dots \dots \dots 5.2$$

Figure 5.24 (a) IPCE spectra of ZnO/CuI, ZnO/FeS₂ and ZnO/FeS₂/CuI photodiode, and (b) responsivity as a function of wavelength of the photodiodes.

Broad peak observed in the IPCE and responsivity spectra around 900 nm corresponds to the contribution due to FeS₂ nanoparticles, as shown in Figure 5.24 (a). Hence, the photodetection in infrared region is also feasible using pyrite in such photodiode configuration. Maximum responsivity of 17 mA/W is obtained at 400 nm as shown in Figure 5.24 (b) with a dotted line.

5.3 Conclusions

The chapter demonstrates that heat treatment of nanocubes in a sulfur atmosphere does not affect the shape and phase purity of hot-injection synthesized nanocubes, and increases the electrical conductivity possibly by removing organic ligands bonded to the facets during the chemical synthesis process.

Band tailing evident in optical absorption of the heat treated pyrite nanocube films corresponds to the behavior of a typical disordered semiconductor. Optical pump-probe transient absorption studies show strong photocarrier generation at the direct band edge of ~ 950 nm. Relaxation of the photoexcited carriers consists of a fast and a slow component. The fast component could be attributed to rapid localization of photoexcited carriers to indirect band edge and shallow defect

states with a characteristic time of 1.8 ps. The slow component could be attributed to carrier relaxation to deep, mid gap states and recombination via direct recombination and hole capture process. The characteristic time for the slow relaxation process was found to be 990 ns.

Temperature dependent electrical transport measurements showed the operation of VRH type conduction mechanism in the temperature range 50 K - 300 K which supports the existence of high density of defect states detected by optical TA measurements.

Temperature dependency of magnetization showed a weak magnetic ordering arising at low temperatures ($< 50\text{K}$), while the behavior at room temperature was clearly diamagnetic, as expected. This change in magnetic ordering at low temperatures could be a manifestation of the sulfur vacancies in the film. These point defects might cluster at low temperatures and behave as though these are localized regions of other iron sulfides which have magnetic ordering such as FeS_{2- δ} ($0 \leq \delta \leq 1$). Such point defects could induce defect states/band within the energy gap that traps the charge carriers by localization and promote recombination. This is the likely reason for the output of photo voltage to be low in devices that use iron pyrite.

We have shown that a photovoltage of 94 mV with current density of 0.4 mA/cm² can still be obtained from heterojunction solar cells with pyrite nanocube films. To increase the efficiency further two issues must be addressed,

- (i) Enhancement of interparticle coupling of the nanocubes or fabricating continuous films,
- (ii) Minimize or control point defects such as sulfur vacancies that appear to be deleterious to charge carrier collection and photovoltage output.

The findings reported in this chapter are previously unexplored photophysics of iron pyrite although they were in the form of nanocube films. They provide deep insight into the intricate relationship between defects (intrinsic and disorder induced) and gap states responsible for photocarrier losses.

This is the first systematic and comprehensive investigation of pyrite photo physics and charge carrier dynamics ever to be reported on iron pyrite.

This chapter also demonstrates the potential of iron pyrite to be used as a photodiode, particularly in the infrared part of the spectrum.

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Chapter 6

Pulsed Laser Deposited Iron Pyrite Thin Films

The pyrite films studied in Chapters 4 and 5 had some disadvantages. The stoichiometry was not easily controllable in the spray pyrolyzed films made in Chapter 4 while the films in Chapter 5 retained their cubic particle nature although they were heat treated to improve the inter-particle interface. Also, their optical and electrical properties showed high defect densities in the film. To offset some of these disadvantages, we chose a well-known, high quality film producing technique to prepare pyrite films and examine their properties. This is Pulsed Laser Deposition (PLD) method. PLD produce, high quality, crystalline films of a material from a target of the same composition.¹ The use of natural pyrite crystal as the target will be examined here which is a novel attempt in pyrite thin film production. Cold pressed pellets of commercial pyrite powder will also be examined as an alternative target. Post sulfurization treatment is usually required to achieve good crystallinity and phase purity In a recent publication H₂S plasma was explored as an alternative route to achieve pyrite film.² In this chapter, we will examine both thermal sulfurization and plasma sulfurization on the PLD deposited films and evaluate their effectiveness by structural and property characterizations. Similar to the films prepared in the previous chapters, the merit of the film will be evaluated on the basis of optical and electrical behavior.

6.1 Experimental Details

6.1.1 PLD film growth procedures

The PLD process set up and its principles are explained in Section 3.1.3. In a typical deposition procedure, the target was placed inside the chamber and the chamber was evacuated to a base pressure below 10^{-7} torr. The glass substrate was cleaned sequentially in DI water, acetone and IPA and then dried. For thermoelectric measurements, quartz substrates were used due to their better thermal insulation which allows us to conduct measurements at low temperatures without having any substrate effects. The cleaned and dried substrate was mounted on the stage and was introduced into the growth chamber through a load lock chamber and its temperature was increased to $100^{\circ}\text{C} - 300^{\circ}\text{C}$ range with a constant ramp rate of $10^{\circ}\text{C}/\text{min}$ by a stage heater. The chamber pressure was then relieved to the growth pressure which was typically in the range $10^{-5} - 10^{-3}$ torr via a gate valve. Deposition at the low pressure range of $\sim 10^{-5}$ torr was done without using any background gas. Substrate to target distance was about 12 cm. Laser fluence from 100 mJ - 300mJ generator was used to grow the film on the substrate. Laser repetition rate was fixed at 10 Hz for all the growth recipes. The substrate was continuously rotated at 2 rpm to ensure uniformity of deposition. After the deposition, the substrate was allowed to cool naturally to room temperature before releasing the vacuum and removing it from the chamber. Figure 6.1 shows the picture of the plasma plume generated when the laser beam incidents on the sample.

Figure 6.1 Photographic image of the PLD plasma plume during laser irradiation.

First trials of PLD were conducted using targets of pyrite pellets made by cold isostatic pressing of the commercial iron disulfide (99.999 % purity, Sigma Aldrich) powder. Cold isostatic pressing was used instead of hot pressing to avoid decomposition of the pyrite while getting a dense and smooth pellet. Subsequently, trials were done by hot pressing also but elemental sulfur powder was added to the commercial powder to compensate for any loss of sulfur during the hot pressing. To prepare target with excess sulfur, the ratio of iron pyrite powder to sulfur powder was taken as 2: 1 (i.e. for 1 gm of pyrite powder, 0.5 gm sulfur powder was added). The surface of the pellets became smoother and denser after hot pressing. Finally, the films were also made using 1 cm³ natural pyrite single crystal (Navajun, Spain) of a cubic shape. Following process parameters were varied and studied for optimization of the film.

- (i) Chamber pressure
- (ii) Laser fluence
- (iii) Substrate temperature

Sulfurization process after PLD deposition was performed. Sulfurization process used in this work will be described as three different type.

(i) Sulfurization in sealed ampoule

PLD deposited films were put in a quartz ampoule loaded with sulfur powder of about 2 mg. (detailed calculation of the sulfur quantity is available in Appendix I). The quartz ampoule was then evacuated to a pressure of about 10^{-3} torr and was sealed using a hydrogen/oxygen torch. The sealed ampoule was then heated in a furnace at 300° C for 2 hrs. Sulfurization in a sealed tube generates constant sulfur partial pressure and under appropriate temperature, it is thermodynamically favorable to achieve phase pure pyrite films. Hence the choice of temperature is important.

(ii) Thermal sulfurization in a tube furnace

The term Thermal sulfurization will be used to refer to the process carried out in a tube furnace at constant N₂ gas flow. This process is similar to the sulfurization processes conducted in Chapters 4 and 5. Sulfur powder was kept at an upstream point in the tube while the film was at the center of the tube at 400° C for 2 hrs. Since, the process is done under constant gas flow of N₂ (~ 20 sccm), sulfur quantity is decided on the basis of sulfurization time. For the all subsequent work presented in this chapter, the quantity of sulfur powder used was around 500 mg for each heat treatment to ensure the adequacy of sulfur to last throughout the duration of the process.

(iii) Plasma Sulfurization

The H₂S Plasma sulfurization process was performed in collaboration with Prof. Colin Wolden (Colorado State University, USA). An inductively coupled plasma source was used to generate the sulfur plasma from H₂S gas. The plasma treatment process was conducted for 60 mins.

For the films deposited directly using natural crystal, a cubic natural crystal was directly used as the target and the film was deposited by laser ablation. Pyrite crystal was diced by a diamond saw and mechanically polished with a grit paper and chemical slurry before the deposition. Deposition was done on glass substrate which was thoroughly cleaned with DI water, Acetone and IPA prior to deposition and loaded to loadlock chamber. Deposition conditions are given in the following table 6.1

Table 6.1 Deposition parameters for thin film PLD growth from pyrite crystal

Base Pressure = 1.8×10^{-7} torr	Laser Energy = 150 mJ
Substrate temperature = 100° C	Repetition rate = 10 Hz
Growth Pressure = 4.2×10^{-6} torr	Deposition time = 12 mins
Target to sample distance = 12 cm	Substrate rotation = 2 rpm

6.1.2 Electrical Characterization

Hall measurements were performed in Van der Pauw configuration as described in section 3.2.3 (a) of Chapter 3. For temperature dependent thermoelectric measurements, films on quartz substrate were used due to provide good thermal insulation.

Temperature dependent transport measurements were performed on thermal and plasma sulfurized film. I-V characteristics were measured in the temperature range 30 K – 370 K using a Keithley source meter and digital multimeter connected to a compressed helium cryostat. Current was applied as the source and the corresponding voltage was measured. Resistance was obtained by taking the ratio of voltage to current at $I = 1 \mu\text{A}$.

6.2 Results and Discussion

6.2.1 Effect of Chamber Pressure on Film Quality

Chamber pressure was varied by controlling the gate valve to bleed argon to raise the pressure to the required value of 5×10^{-3} torr. The morphology of the film obtained was found to be rough with many spherical particles on the surface as shown in Figure 6.2.

Figure 6.2 (a) SEM image of surface morphology of PLD deposited film and (b) EDS elemental mapping of Fe and S in the selected area of the film.

Figure 6.2 (b) shows the energy dispersive spectra (EDS) elemental mapping of the selected area of the film. It can be seen that Fe and S distribution is uniform in the film.

Figure 6.3 shows the Raman spectra of the film. The Raman spectrum features a broad spectrum with peaks at 342 cm^{-1} and 377 cm^{-1} wavenumbers for the as-deposited PLD films. These peak positions correspond to those of pyrite.³ However, the peak width being substantially broad indicates the amorphous nature of the film. Reducing the chamber pressure did not result in any change in the Raman spectra and the film remained amorphous.

Figure 6.3 Raman spectra of PLD film deposited at 300 mJ laser fluence on a glass substrate.

Figure 6.4 shows the SEM images of the surface morphology of the films deposited on glass substrate for 30 mins at two different chamber growth pressures of 1×10^{-3} torr and 1×10^{-4} torr while keeping the substrate temperature constant at 100°C .

Figure 6.4 SEM image of the surface morphology of the PLD films grown at (a) 1×10^{-3} torr chamber pressure (b) 1×10^{-4} torr chamber pressure. The lower row shows the corresponding image at higher magnification.

It is evident from Figure 6.4 that the film is composed of spherical particles on the substrate. This particle formation during PLD process is discussed in Chapter 3 section 3.1.3 (b) as “splashing effect”. Reducing the chamber pressure from 10^{-3} torr to 10^{-4} torr results in smoother films with less particle formation at the

surface. Hence chamber pressure below 10^{-3} torr is desirable to grow smoother films. However, extra techniques may be required to completely eliminate the particles as discussed in Chapter 3.

6.2.2 Effect of Laser Fluence on Film Quality

Laser fluence was varied from 300 mJ to 50 mJ. Figure 6.4 shows the SEM micrographs of the PLD films deposited under same chamber pressure of 6×10^{-5} torr at different laser fluence powers. Varying the laser fluence power did not reduce the splashing effect. Morphology appears to be similar for all the films, as shown in Figure 6.5. However, reducing the laser fluence seems to result in the smaller particle formation at the surface. PLD laser specifications allowed to go to minimum of 50 mJ laser fluence, therefore 50 mJ was the lowest laser fluence used. Raman spectra of the PLD deposited films at different laser fluence are shown in Figure 6.6. Film quality and phase remained insensitive to laser fluence. Irrespective of laser fluence, all films showed broad peaks in Raman spectra indicating the amorphous nature of the film.

Figure 6.5 SEM images of PLD films deposited at laser fluence of (a) 50 mJ, (b) 100 mJ, (c) 150 mJ, (d) 200 mJ, (e) 250 mJ and (f) 300 mJ.

Figure 6.6 Raman spectra of the pyrite PLD films deposited on glass substrate at different laser fluence power.

6.2.3 Effect of Substrate Temperature on Film Quality

Films were deposited at different substrate temperatures. Films were deposited at $10^{-4} - 10^{-5}$ torr chamber pressure and substrate temperatures of 100° C, 200° C and 300° C. SEM images of the films are given in Figure 6.7, showing that the surface looks similar with spherical particles on the surface. Raman spectra of the films are shown in Figure 6.8. Increasing the substrate temperature did not show any marked difference on the film quality.

Figure 6.7 SEM image of the PLD films deposited on glass substrate at temperatures (a) 100° C, (b) 200° C and (c) 300° C.

Figure 6.8 Raman spectra of PLD pyrite films deposited at substrate temperatures of (a) 100° C, (b) 200° C and (c) 300° C.

6.2.4 Sulfurization of PLD Film made from Synthetic Target

In order to convert the amorphous thin films prepared by PLD to crystalline single phase pyrite, heat treatment was conducted in a sealed ampoule. Pyrite thin film was deposited on quartz substrate at 100° C for 30 mins and subsequently sulfurized in quartz ampoule (See Section 6.2.1 and Appendix I). Sealed ampoule was heated at 300° C in a furnace for 2 hours.

Figure 6.9 Raman spectra of the target, as-deposited film, and the film after ampoule heat treatment.

After heat treatment, sharp peaks at 341 cm^{-1} and 379 cm^{-1} corresponding to pyrite phase appear, as shown in the Figure 6.9. Hence the heat treatment process converts the amorphous films into crystalline single phase pyrite films. Thus, the sulfurization process is necessary to obtain pyrite films after PLD deposition. Sulfurization procedures used in Chapters 4 and 5 are different from this ampoule sulfurization. Sulfurization in a sealed ampoule maintains constant sulfur partial pressure that favors grain growth while maintaining the stoichiometry of the film. Also, 300°C sulfurization temperature is sufficient for the crystallization to occur. Direct in-situ conversion might be possible if PLD deposition is done under sulfur gas ambient (for example H_2S) but the PLD system used in this study was not equipped to handle sulfur containing gases.

6.2.5 Electrical Properties

Hall and Seebeck measurements were carried out on the films. Hall measurements conducted on the heat treated films showed p-type conductivity with carrier concentration of 10^{18} cm^{-3} , similar to the pyrite films prepared in Chapters 4 and 5. For Seebeck measurements, films deposited on quartz substrate were used to provide good thermal insulation. Room temperature Seebeck measurements gave a positive Seebeck coefficient (σ) of $65\text{ }\mu\text{V/K}$ supporting p-type conductivity (see section 3.2.4 of Chapter 3 for the theory). Since the thermoelectric measurements are bulk sensitive, indication of p-type conductivity from Seebeck coefficient measurement confirms that the dominant charge carriers are holes as obtained by the Hall measurements. As discussed in the theory of thermoelectric transport in Chapter 3 Section 3.2.4, temperature dependent Seebeck measurements give insights on the scattering mechanism and transport in the film. Hence, this was done by ramping down the temperature from 340°C to 160°C . The results are shown in Figure 6.10. Three points were measured at every temperature.

Figure 6.10 Temperature dependent Seebeck coefficient of sulfurized pyrite PLD film deposited on quartz substrate.

From Figure 6.10, it is clear that σ remained positive throughout the temperature measurement range. The experimental data could be fitted to a straight line. Linear variation of σ with temperature is an indication of a degenerate semiconductor. Hence the carrier concentration of 10^{18} cm^{-3} obtained by Hall measurement, which is higher than the normal ($10^{15} - 10^{16} \text{ cm}^{-3}$) for a semiconductor with 1 eV band gap, is in agreements with the degenerate semiconducting behavior indicated by the linear temperature dependence of Seebeck coefficient. This outcome generally agrees with the deductions made in Chapters 4 and 5 on pyrite thin films fabricated by different techniques. This ubiquitous electrical behavior of the pyrite thin films is independent of the fabrication method. Hence, it is possible that the electrical properties of pyrite thin films are dominated by intrinsic rather than the extrinsic factors.

6.2.6 Elemental Analysis using RBS

Rutherford Backscattering Spectroscopy was conducted on the film sample to determine elemental composition and the prevailing Fe: S ratio. In this method, He^{++} particles with energy of 3.034 MeV hit the target and lose their energy by scattering by the atomic species present in the film. Thus, the signature of heavier element appears at substantially higher channel no. in the spectrum. In the course of their travel, He^{++} ions lose their energy with depth of penetration. This makes the RBS technique depth sensitive. For the RBS spectrum in this study, incident He^{++} ion beam was impinged on the film at an entrance angle of +7 degree, the scattering angle was 173 degrees and the detector resolution was 15-20 keV. Simulation of the spectra done by the software is on the basis of calculation of scattering cross-section, stopping power and energy loss straggling for a hypothetical slab of particular elements present in the film.⁴ The peak corresponds to the energy spread of ion due to scattering from a particular element in a sample of certain thickness. Figure 6.11 shows the RBS spectrum of a film.

Figure 6.11 RBS spectra of the sulfurized film on the quartz substrate.

Two peaks corresponding to Fe and S are clear in Figure 6.11. Fe: S stoichiometry close to 1:2 obtained from RBS spectra by simulating the spectra using SIMNRA RBS data analysis software. The spread in Fe and S peaks in the RBS spectra indicates that the films are quite rough.

6.2.7 Pyrite film deposited from Natural Single Crystal

Films deposited directly from the natural crystal target were found to be amorphous similar to the films made from synthetic target prepared from commercial powder. Therefore, we resorted to sulfurization process in a tube furnace described in Section 6.2 (ii) which is similar to the processes used in Chapters 4 and 5.

6.2.7.1 Thermal and Plasma Sulfurization

Sulfurization process was conducted to convert the amorphous films to high quality and single phase films. We examined the effect of thermal sulfurization process using elemental sulfur powder and H₂S plasma sulfurization. Thermal sulfurization process is diffusion limited process and there are many reports that claim incomplete conversion of any unwanted Fe-S phase that may be present in the film to pyrite phase.^{3,5} On the other hand, sulfur plasma generated from ionizing H₂S gas is more reactive than thermally evaporated sulfur powder and has shown to be more efficient in converting sulfur deficient phases to the pyrite phase.² Therefore, we decided to examine the impact of both sulfurization processes on the optoelectronic properties of the PLD films. Two as-deposited films were heat treated in a quartz tube furnace and H₂S plasma separately. The procedures are described in Section 6.2. After the thermal and plasma sulfurization, both the films were characterized by various techniques. This will be discussed in subsequent sections.

6.2.7.2 Film Morphology and Phase Analysis

Figures 6.12 (a) and (b) show the SEM images of the thermally and plasma sulfurized films respectively.

Figure 6.12 SEM image of top surface of (a) Thermally sulfurized film and (b) Plasma sulfurized film. Respective high magnification images are shown below with 200 nm scale bar.

Thermal sulfurization process results in a bigger particle size formation, as shown in Figure 6.12 (a) giving a rougher surface while plasma sulfurized film appeared to be a bit smoother, as shown in Figure 6.12 (b). Spherical particles can be seen at the surface due to the laser splashing effect. Figure 6.13 shows the cross section SEM image of thermally and plasma sulfurized samples. Cross-section SEM in Figure 6.13 shows film thickness to be around 50 nm for both thermally sulfurized and plasma treated films.

Figure 6.13 SEM image of the cross section of (a) thermally sulfurized and (b) plasma sulfurized thin film.

Phase purity of both the films was examined by Raman spectroscopy. Figure 6.14 shows the Raman spectra of both the samples.

Figure 6.14 Raman spectra of the natural single crystal target, as-deposited PLD films, thermally sulfurized film and H₂S plasma sulfurized thin film.

For the plasma treated film, a small extra peak is visible at 324 cm⁻¹. This corresponds to the marcasite phase. This indicates the presence of marcasite as a secondary phase in the plasma treated film. However, it is difficult to quantify the marcasite content from the Raman spectra. Further, increase in the duration of plasma sulfurization did not eliminate the marcasite impurity. It must be noted that the thermally sulfurized film shows no marcasite peak in the Raman spectra, as evident in Figure 6.14. Examination of the spectrum for the target crystal also indicates only the pure pyrite phase. Hence, marcasite was not present in the target. Figure 6.15 shows the schematic of the thermal and H₂S plasma sulfurization process and the final product. Appearance of marcasite was unexpected; it was not detected in any of the films fabricated by other methods reported in Chapters 4 and 5. According to reports in the literature this is an undesirable phase for photovoltaic applications and is considered to be one of the root causes for the low photovoltage generation in pyrite-based devices.

Figure 6.15 Schematic of the film conversion from thermal and H₂S plasma sulfurization process.

6.2.7.3 Elemental Analysis using RBS

RBS measurements were carried out on thermally sulfurized and plasma treated films to analyze elemental composition and determine the prevailing Fe: S ratio. Figure 6.16 shows the RBS spectra obtained. Simulation of RBS spectra was performed as described in section 6.4.2. Fe: S ratio for both thermal and plasma sulfurized film was found to be stoichiometric at 1:2. However, a small additional peak was detected in Figure 6.16 corresponding to Ca. This Ca impurity might have come from the natural single crystal target itself even though it was not detected by Raman spectroscopy. Since the width of the Fe and S peaks in the RBS spectra are quite similar, no significant difference in the film morphology is expected.

Figure 6.16 RBS spectra of thermal and plasma sulfurized PLD thin film.

6.2.7.4 Optical Absorption and Band Gap

Optical absorption of the thermal and H₂S plasma sulfurized films were measured using UV-Vis spectrometer. Band gap is calculated using the Tauc plot analysis of the optical absorption. Figure 6.17 (a) shows the optical absorption characteristics of the thermal and plasma sulfurized films.

Figure 6.17 (a) Optical absorption spectra of thermal and plasma sulfurized PLD films. and (b) transmission, reflection and absorption spectra of thermally sulfurized film.

The optical absorption spectra appear similar in both the films. Both sulfurization methods gave very similar films except that a small trace of marcasite was detected in the plasma sulfurized film. Since marcasite is reported to be a low band gap phase,⁶ similar absorption spectra for both films were not anticipated. However, since the spectra obtained are similar it seems that the amount of marcasite was inadequate to influence the absorption characteristics of the whole film.

The band gap was analyzed by Tauc plot analysis. Figure 6.18 shows the band gap of thermal and H₂S plasma sulfurized films.

Figure 6.18 Band gap determination from Tauc plots of (a) thermally sulfurized and (b) plasma sulfurized films.

The experimental data for the two films fitted well with a direct band gap equation in the Tauc plot and the band gap values were estimated to be 1.01 eV and 1.05 eV for the thermally sulfurized and the H₂S plasma treated films, respectively, as shown in Figure 6.18 (a) and (b). Again, the band gap seems to be insensitive to the presence of marcasite phase impurity at the levels present in our film. This indicates that the amount of marcasite phase is small and, thus, the band edge optical transitions are predominantly due to the pyrite bands and intrinsic defects/disorders might be responsible for the significant absorption below the band gap. Another possibility is that band gap of marcasite itself might be close to that of pyrite.

There is a little consensus in the literature regarding the effect of marcasite impurity in pyrite. Generally, marcasite impurity is considered detrimental to the photovoltaic effect due to its low band gap of 0.34 eV.⁶ In this work, the presence of marcasite in one pyrite thin film has not shown to exhibit any difference in the electrical properties. This creates the doubt whether marcasite is detrimental to pyrite or whether the internal disorder in pyrite itself is the detrimental factor. To add to this uncertainty, a recent DFT calculation and experimentation claim that the band gap of marcasite is close to that of pyrite, in stark contrast to the earlier reports that indicated a very low band gap for marcasite.^{5,7} Our experimental results possibly support the claim of similarity in band gaps of the two phases. Sub bandgap absorption caused by crystal defects makes it difficult to predict the true band gap of the pyrite from Tauc plots. The band gaps estimated for the both the films in our study are very similar, suggesting that the marcasite and pyrite phases possibly have band gap values close to each other. However, it is to be noted that the marcasite content in the film is an important factor that might affect the optical absorption characteristics. If the content is too small, the effect may not be detectable even if marcasite has a band gap very different to that of pyrite. The films in our study were too thin to get any reliable data by XRD to quantify the phase contents. In a similar study comparing pure pyrite films with pyrite-marcasite mixed phase films where the second phase content was 10 – 50 vol %, showed no significant difference in absorption feature in the films.⁵ Also, the marcasite phase did not affect the nature of optical absorption. This point is supported by the direct band fit of the optical absorption. The direct band gap fit is similar to the optical transitions observed for the thin films prepared in Section 4.2.4 of Chapter 4 and Section 5.7 of Chapter 5. Defects and disorder in the pyrite form electronic bands near the band edges and results in direct optical absorption rather than the indirect. This is analogous to the thin films prepared in Chapter 4 and 5. Thus the intrinsic disorder in the pyrite itself seems to form the defect bands and remains unaffected by the presence of marcasite phase.

6.2.7.5 Electronic Properties and Charge Transport Measurements

Hall measurements were performed to investigate the number of charge carriers and their type. Measurements were performed in Van der Pauw configuration. Table 6.2 shows the measured Hall parameters for thermal and plasma sulfurized thin films on glass substrate.

Table 6.2 Hall parameters of thermally and H₂S plasma sulfurized PLD thin films on glass substrate.

Parameters	Thermally Sulfurized	Plasma Sulfurized
Carrier type	p-type	p-type
Carrier density (cm ⁻³)	7 x 10 ¹⁸	4 x 10 ¹⁹
Mobility (cm ² /V-s)	1.4	0.3
Resistivity (Ω-cm)	0.54	0.37

The data in Table 6.2 shows high charge carrier concentration and low carrier mobility for H₂S plasma sulfurized sample. Thermoelectric measurements were performed as a complementary technique to probe the charge carrier type. Room temperature Seebeck coefficient for thermal and H₂S plasma treated films found to be ~ + 74 μV/K and + 62 μV/K respectively. These values of Seebeck coefficient are not very different and nothing can be said regarding electronic behavior of the films on the basis of this small difference. Positive Seebeck coefficient for both the films confirms the charge carrier type to be holes, similar to the observation from Hall measurements. Plasma sulfurized sample possess higher conductivity than thermally sulfurized film. Both films showed no resistance change upon light illumination proving lack of photoactivity. So the films were degenerate with high hole concentration and no photoactivity.

Figure 6.19 shows the transport measurement plots analyzed by fitting $\ln R$ and temperature with equations corresponding to thermally activated transport Equation 3.11 and Mott-VRH transport Equation 3.12.

Figure 6.19 Temperature dependent electrical transport measurements of thermal and plasma sulfurized PLD thin film, (a) $\ln R$ vs $1/T$ plot and activated transport fit (black lines) and activation energies, (b) $\ln R$ vs $T^{-1/4}$ plot and Mott-VRH transport fit (black lines).

Figure 6.19 (a) shows the plot for a conventional diffusive transport. Linear region can only be obtained at the higher temperature (black line in the curve). Slope of the linear fitted line was used to calculate the activation energy by Equation 6.1

$$E_A = \text{Slope} * k_B \dots \dots \dots 6.1$$

where, k_B is the Boltzmann constant (8.617×10^{-5} eV/K)

Thermal activation energy for thermally sulfurized and H_2S plasma sulfurized films were obtained as 49 meV and 37 meV respectively. Activation energy for a conventional band to band transport corresponds to the thermal activation of the carriers from the defect level close to the band edges. Activation energy obtained in this case is close to the activation energy values for thin films prepared in Chapter 4 (39 meV) and Chapter 5 (87 meV). Slightly lower value of

activation energy for plasma sulfurized film reflects a higher defect density in this film. However, it is not clear whether this could be attributed to the marcasite phase impurity. So it is possible that the higher conductivity from marcasite containing film might come from the thermal activation of the carriers from additional energy states formed due to the presence of marcasite phase which will create a new type of defect in the film namely, the pyrite-marcasite interface. In Figure 6.19 (a), decreasing the temperature leads to the deviation of the curve from the straight line, an indication of the onset of different conducting mechanism. The data fits well with the hopping transport equation (Equation 3.12, Chapter 3) for temperature below 250 K. Figure 6.19 (b) shows the $\ln R$ vs $T^{-1/4}$ plot. The relation is a characteristic of Mott-variable range hopping transport (Mott-VRH). Good straight line fit is obtained for both the curves on a wide temperature range. For plasma sulfurized sample, hopping transport extends more from 60 K – 250 K while for thermal sulfurized film, hopping transport is from 90 K – 250 K. Decreasing the temperature further leads to the deviation of the curve from straight line which might be due to some different transport mechanism coming into operation.

Mott-VRH hopping for both the samples over a wide temperature supports the presence of high density of localized energy states. Characteristic temperature (T_0) for thermal and plasma sulfurized films was calculated to be around 8.8×10^5 K and 4.7×10^5 K respectively. Such high characteristic temperatures indicate high density of localized gap states and small localization lengths. It should be emphasized here that Mott-VRH type conduction is observed for the films prepared in Chapter 4 and 5 as well for temperature below 250 K. So the PLD grown pyrite films show electrical characteristics similar to other films studied here, regardless of the preparation method. Thus, the impact of intrinsic disorder in pyrite is the significant factor that severely impacts on the electrical properties of pyrite thin films.

6.3 Conclusions

- Iron pyrite thin films were successfully grown by pulsed laser deposition and subsequent sulfurization treatment.
- Feasibility of direct PLD deposition of thin films from natural pyrite single crystal target was demonstrated.
- Thermal sulfurization of thin films using elemental sulfur yields single phase pyrite films while H₂S plasma sulfurization leads to some marcasite impurity.
- The band gap of iron pyrite in these thin films was found to be insensitive to the presence of marcasite phase impurity. No photo response was observed in all the films examined in this chapter.
- Both thermally sulfurized and plasma sulfurized films showed p-type degenerate conduction behavior. Marcasite containing film was found to be electrically more conducting than the thermally sulfurized film with a higher hole carrier concentration of $\sim 10^{19} \text{ cm}^{-3}$.
- Mott-VRH conduction was observed over a wide temperature range of 90 K – 250 K for thermally sulfurized film, and 60 K – 250 K for plasma sulfurized film, indicating a high density of defect states. The range 300 K – 370 K is characterized by thermally activated transport.
- The results indicate that the intrinsic defects in pyrite alone cause a severe impact on the electronic properties of the material. Pure phase pyrite films do not guarantee a good optoelectronic performance.

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Chapter 7

Study of Pyrite Natural Single Crystal

Availability of large pyrite single crystals naturally from the mines has facilitated research in single crystals which offer a great opportunity to explore their bulk properties. Recent research on pyrite single crystals has revealed carrier inversion at the surface. The problem is stated as formation of a surface inversion layer and fermi level pinning at the surface of single crystals. This chapter deals with the study of natural single crystals in the context of this project which mainly deals with thin films. Single crystals are characterized for crystallinity, phase purity and then a special experiment is designed to investigate possible surface inversion. Temperature dependence of resistance at low temperature under different measurement configurations reveals the surface to be more conducting than the bulk at low temperatures. This may signify the existence of a surface inversion layer on pyrite single crystals at very low temperatures.

7.1 Introduction

Large single crystals of pyrite are easily available from natural sources. Previous works on natural single crystals have shown some photoactivity which encourages us to re-evaluate them here. The photovoltaic performance of pyrite crystals was low, as in the case of thin films discussed in Chapters 4, 5 and 6. Single crystals also could have the same crystal defects to which the low photovoltaic performance of thin films was attributed to in previous chapters, namely sulfur vacancies. Besides, naturally occurring crystals are prone to impurity elements and inclusions which could add to the carrier transport complications. In addition, previous researchers who examined single crystals have proposed a possible, additional complicating phenomenon called “Surface Inversion”.¹⁻³ In Surface Inversion in a semiconductor, the surface charge carriers become opposite to that of the bulk. For example, n-type carriers on the surface and p-type carriers in the bulk or vice versa. In iron pyrite, it was proposed that p-type surface layers form due to fermi level pinning at the surface causing the energy bands to bend upwards and create a larger number of holes at the surface while the bulk remains n-type.¹ This makes the bulk and the surface to have different conductivities. This phenomenon is not specific to pyrite; even other semiconductors such as InN and HgTe are reported to exhibit such inversion layers at the surface.⁴

There is no direct experimental method to detect surface inversion layers. Most researchers rely on a combination of techniques such as photoelectron spectroscopy, surface potential measurements, thickness dependent conductivity measurements, Mott-Schottky analysis etc. to argue, indirectly, the existence of such a layer. In the present work reported in this chapter, an attempt is made to directly measure the difference in the bulk and surface conductivities. Design of a special experimental technique is required to achieve this. The experimental design used in this work is adapted from the works of Wolgast et al, and Shekhar

et al, on SmB_6 and $\text{Bi}_2\text{Te}_2\text{Se}$ single crystals respectively, which are “Topological Insulators” (TI) that are known to have a conducting surface and an insulating bulk.^{5,6} Comparison of the surface and bulk resistances measured by this technique in the present work on a pyrite crystal seems to indicate a significant difference at low temperatures. Our work reported in this chapter is the first attempt by anyone to measure the difference between surface and bulk conduction on pyrite. The results obtained from this special experiment, along with conventional characterization results will be presented and discussed in this chapter.

7.2 Experimental Details

7.2.1 Crystal Preparation for Characterization

The natural crystal used in this project is from Navajun, Spain. The crystal is a cube of side length approximately 1 cm. It was diced by a diamond saw into square wafers of 1 mm thickness. The wafers were polished to remove any surface artifacts caused by diamond saw cutting. All subsequent characterizations were performed on polished pyrite wafers. Figure 7.1 shows a schematic of the crystal dicing method and its crystallographic orientation along with the configuration in which the different characterizations were performed. For electrical transport measurements, contacts were made on both sides of the pyrite wafer to facilitate measurements in different contact geometries. This will be discussed in detail in Section 7.2.2.

Figure 7.1 Schematic of the crystal cutting, sample preparation and configuration for different characterization.

7.2.2 Experiment Design for Electrical Transport Measurements

The reason for this experiment design is to enable the measurement of temperature dependence of bulk and surface resistances. To do this, measurements must be taken in different electrical cum geometrical configurations to be able to separate the two resistances by compelling the current to take different paths through the wafer. Such measurements have been conducted recently on SmB_6 and $\text{Bi}_2\text{Te}_2\text{Se}$ single crystals which are topological insulators.^{7,8} These compounds are known to exhibit certain surface electronic states which make the surface conducting and the bulk insulating. There exist few reports on the attempt to deconvolute the bulk and surface conductivity components by measuring temperature dependence of resistance in different contact configurations but none on pyrite or other sulfides that show photovoltaic activity.⁶ The similarity of the difference between surface conductivity and bulk conductivity in topological insulators and pyrite may allow us to use the same techniques to study pyrite. Although the difference in bulk and surface conductivity in SmB_6 is due to different reason, the effect is similar to that of pyrite surface and bulk conductivity. Therefore, the experiment design used here

is adapted from that of topological insulators used by Wolgast et al. and Shekhar et al. reported in the literature.^{5,6} We will discuss the three electrical configurations and their geometries chosen in this study in the following paragraphs.

The device was made by cutting the 1 mm thick wafers to fit into a commercial chip carrier made to take chips of size $1 \times 1 \text{ cm}^2$ as shown in Figure 7.2. Top and bottom electrodes were made by thermally evaporating 100 nm thick Al layer first followed by another 100 nm thick Au layer. The Au layer is to protect the Al layer from oxidation while the latter is to form an ohmic contact with pyrite. Top contact electrodes were made by directly evaporating the metals sequentially on the wafer surface while the bottom electrodes were made similarly on a 300 nm SiO_2/Si wafer to fit into the same chip carrier as a bottom support to the pyrite wafer. The Si wafer was cleaned using DI water and IPA prior to the electrode deposition. The pyrite wafer with top electrodes was then placed on the Si wafer and glued appropriately using a conducting epoxy and cured at 120°C . Subsequently all electrical connections were made by wirebonding the top and bottom electrodes to the chip carrier electrical contacts. Chip carrier was then placed in a vacuum chamber connected to a cryostat. Figure 7.2 shows the picture of the wirebonded contacts of the pyrite wafer mounted on the chip carrier. The electrical readouts were taken from a Keithley source meter and a digital multimeter and the temperature was controlled by a Lake Shore temperature controller. The measurement was recorded in the temperature range 30 K – 350 K by a LabVIEW program.

Figure 7.2 Diced single crystal mounted on a chip carrier and wirebonded top and bottom contacts.

The experiment is designed to measure the electrical resistance when a steady current flows along different paths in the pyrite wafer in different geometrical arrangements. This is achieved by choosing different combinations of top and bottom electrodes as current and voltage terminals. A steady current was applied by a current source (I) and the resulting potential difference (V) between specific contact electrodes was measured. Initially, full I - V characteristics of the sample were mapped and a suitable current was chosen to ensure the characteristic is in the linear region. A current of $1\ \mu\text{A}$ was found to be suitable. Subsequently the resistance was calculated at $I = 1\ \mu\text{A}$ current for the different configurations used.

Figure 7.3 schematically shows the three different configurations of the electrodes used in this study. Out of the eight electrodes available, four will be used for any one configuration. The current is passed between two contacts shown as I_+ to I_- in Figure 7.3 and corresponding potential drop is measured by a high impedance voltmeter across the contacts V_+ and V_- . Subsequently resistance R could be calculated using Ohm's law.

Figure 7.3 Four probe I-V measurement in different resistance measurement configuration.

The three configurations will be termed “Top”, “Bottom” and “Hybrid” as shown in Figure 7.3. In the Top configuration, the current of $1 \mu\text{A}$ is applied across contacts 1 and 4 and the corresponding potential drop is measured across contacts 2 and 3. This is similar to a conventional four point probe method of measuring resistance. In the Bottom configuration the current is applied across contacts 1 and 4 and the corresponding potential drop is measured across contacts 6 and 7 on the reverse of the wafer. In the Hybrid configuration, current is applied across contacts 1 and 5 and the corresponding potential drop is measured across contacts 2 and 6. The measurements were taken for many temperatures at 10 K interval from 30 K – 340 K for all three configurations.

7.3 Results and Discussions

7.3.1 Crystal Structure and Phase Analysis

X-ray diffraction of the diced single crystal was performed by placing the wafer flat on the sample mounting stage with [100] direction normal to the horizontal stage. Its XRD spectrum was measured in a thin film attachment on the (100) surface of the wafer. The pole figure was also obtained to confirm the crystallographic orientation of the wafer. Figure 7.4 shows the XRD data and the pole figure of the sample.

Figure 7.4 (a) XRD of the polished crystal surface in thin film attachment, (b) pole figure measurement along (100) direction.

XRD of the crystal surface shows only a single peak corresponding to (100) plane as shown in Figure 7.4 (a). Sharp peak with low FWHM exemplifies a large single crystal sample in comparison to the polycrystalline thin films studied in Chapters 4 and 5. Pole figure in Figure 7.1 (b) also shows the intensity only at the [001] pole. These confirm that the wafer is a single crystal and its face is a (100) plane.

Figure 7.5 Raman spectra of the pyrite single crystal.

Raman spectrum of the crystal was measured using 532 nm laser. Figure 7.5 shows the Raman spectra of the single crystal. All the peaks correspond to the pyrite phase. E_g , $T_g(1)$, A_g and $T_g(3)$ phonon modes can be clearly seen in the spectra. Interestingly, Raman spectra measured for thin films in Chapter 4, 5 and 6 showed only three phonon modes A_g , E_g and $T_g(3)$. $T_g(1)$ phonon mode in Figure 7.5 in addition to other three modes implies the better crystalline quality than the thin films. Also, high Raman intensity and narrow peak width (FWHM) indicates the high crystalline quality of the sample.

7.3.2 Crystal Surface and Chemical Analysis

SEM micrograph of the surface of the polished wafer is shown in Figure 7.6. It is clear from this figure that surface looks quite rough with remnant scratches from the polishing. EDS spectra were captured from the different areas of the sample and are also shown in Figure 7.6.

Figure 7.6 Top-view SEM image of the polished crystal surface and the corresponding EDS elemental mapping and S: Fe stoichiometry.

Only the Fe and S peaks were detected by EDS and corresponding peak ratios from different areas are also indicated in Figure 7.6. In all the cases, S:Fe ratio is close to the expected value of 2 which indicates chemical homogeneity but, EDS is not very accurate for quantitative chemical analysis, particularly when a light element such as sulfur is involved. It is important to note that no impurity peaks were detected which proves that the pyrite crystal is pure.

To quantify the stoichiometry of Fe and S precisely, RBS spectrum was taken on the wafer. RBS is very sensitive to heavy and light elements and is particularly very sensitive to Fe compounds.

Figure 7.7 RBS spectrum of the diced and polished wafer.

Figure 7.7 shows the RBS spectrum of a thick (~ 1 cm) crystal. Peaks corresponding to Fe and S are shown in the figure along with the simulated curve to obtain best fit to the experimental data. The best fit is obtained for S:Fe = 2 which is close to the ideal stoichiometry for pyrite. This proves that the sample is a single crystal, single phase and is stoichiometric.

7.3.3 Hall Measurements

Hall measurements were conducted on the polished wafer in Van der Pauw geometry as explained in Chapter 3. Table 7.1 shows the Hall parameters obtained

Table 7.1 Hall parameters for single crystal pyrite wafer

Parameter	Value
Carrier type	electrons
Carrier concentration (cm ⁻³)	5.18 x 10 ¹⁶
Mobility (cm ² /V-s)	64.9
Resistivity (Ω-cm)	1.8

From Hall measurements, the sample was confirmed to be n-type and with a high mobility, contrary to thin films that possess p-type conductivity and low mobilities (refer to section 4.2.5, 5.6 and 6.4.1 of Chapter 4,5 and 6 respectively. This is in agreement with the previous work done on single crystals.^{1,2} As shown in Figure 2.6 of Chapter 2, single crystals tend to be n-type with high mobilities. The natural crystal studied in this project lies in the same region in a carrier concentration vs mobility plot as other crystals reported in the literature, as shown in Figure 2.6 of Chapter 2. The possibility of a p-type surface inversion layer existing on n-type crystal has been discussed in recent publications.^{2,4,9} Temperature dependent Hall measurement of a n-pyrite single crystal showed the onset of p-type behavior at low temperatures of around 120 K – 150 K. p-type behavior at low temperature was attributed to the surface conduction which was corroborated by temperature dependent electrical transport measurements.¹ Since in their study, surface conduction starts to dominate at low temperature, temperature dependent measurements are important. So these crystals are suitable to conduct electrical measurements to investigate surface and bulk conductivity.

7.3.4 Temperature Dependence of Electrical Resistance

Temperature dependent electrical transport measurements were performed on the crystal in top, bottom and hybrid configurations in the temperature range of 30 K – 350K, as shown in Figure 7.3. Resistance at different temperatures was measured. Resistance in the top, bottom and hybrid configuration will be referred as R_T , R_B and R_H respectively, in this section. Figure 7.8 shows the resistance vs. temperature plot for all three configurations.

Figure 7.8 Resistance vs. temperature for three configurations; top, bottom and hybrid.

From Figure 7.8, as the temperature is decreased, resistance in individual configuration increases, similar to a typical plot for semiconductors. Resistance in hybrid configuration (R_H) starts to increase more at temperature below 120 K while resistance in top (R_T) and bottom (R_B) remains almost steady.

The resistance change with temperature in relation to bulk and surface conduction can be understood as following

- When the bulk conduction dominates

$$R_T \sim R_B > R_H$$

This is because the current would simply flow through the bulk homogeneously and not through the surface, so the resistance measured across R_H would be very small. The condition is schematically shown in Figure 7.9.

Figure 7.9 In hybrid configuration, current applied across I_+ and I_- terminal and voltage is measured at terminal V_+ and V_- . Red arrow indicates the flow of current within the bulk.

- When the surface conduction dominates

$$R_H > R_T \geq R_B$$

Since the major current path would be the surface, R_H would dominate. The reason why R_T would be higher than R_B is because the current in the top configuration would be higher across V_+ and V_- terminal than in the case of bottom configuration for R_B . Schematic of the current flow in hybrid configuration is shown in Figure 7.10 when surface conduction dominates.

Figure 7.10 In hybrid configuration, current applied across I_+ and I_- terminal and voltage is measured at terminal V_+ and V_- . Red arrow indicates the flow of current. Current flows through surface when surface conduction dominates.

Any difference in measured resistances of the three configurations indicates that the surface and bulk conductivities are different. The results plotted in Figure 7.8 shows that for the top and bottom configurations, the measured resistances $R_T \sim R_B$, while in the hybrid configuration resistance starts to increase as the temperature is decreased below 150 K. Previous studies on pyrite synthetic crystals by Law et al. showed resistance increase at a similar temperature which they argued to be due to the surface inversion layer.¹ From the above two conditions on bulk and surface conductivity difference, our results seem to indicate that the surface conduction dominates at temperatures below 150 K. Higher resistance in the case of hybrid configuration than top and bottom configurations may be due to the longer current path when the surface conductivity starts to dominate. However, above 150 K, the resistance in all three configurations are similar and no observable difference is found between the surface and bulk conductivities. At temperature above 150 K, the electrical transport is a complex function of both the surface and the bulk resistances and the present data in Figure 7.8 does not elucidate this. If there is no difference between the bulk and the surface conductivities, then R_T and R_B would be similar while R_H would be the different. The condition $R_H > R_T \geq R_B$ is observed at low temperatures which implies that at low temperatures the surface conduction dominates as the bulk becomes more and more insulating with decrease of temperature.

Our results support the condition $R_H > R_T \geq R_B$ at low temperatures which is the case for dominant surface conduction. Similar measurements performed on SmB_6 single crystals also showed such resistance dependence on temperature at the same measurement configuration used here. It was attributed to surface conduction due to topological surface states which were responsible for increased surface conductivity.¹⁰ Such excess surface conductivity was also observed in the case of InN film. It was found that carrier concentration at the surface and bulk is different and the phenomena was attributed to charge accumulation layer at the surface.¹¹ The results in the present case of iron pyrite might be due to the

surface inversion layer on the pyrite crystal. Recent measurements also revealed surface states on a pyrite nanoplate sample supporting the claim of the presence of inversion layer.⁹ These results are the direct experimental proof of the surface and bulk conductivity difference and support the surface inversion layer hypothesis in iron pyrite single crystals at low temperatures. Also, the simplicity of the experiment makes it applicable to different semiconductors as well to study their surfaces.

7.3.5 Does Surface Inversion Exist?

Our results do not imply that the difference between the surface and bulk conductivity is due to a surface inversion layer. There could be many reasons for the aforementioned phenomena. We will discuss all the possibilities in this section. The possible explanations could be given on the basis of following arguments

- (i) **Extrinsic impurities/dopant** – Conductivity of a crystalline semiconductor is influenced by the intrinsic charge carriers and extrinsic impurity.¹² Former is due to native defects and presumably not responsible for governing electrical properties of pyrite. Extrinsic impurity causes the defect states to form near the band edges and may affect the conductivity.¹³ For pyrite, commonly expected extrinsic dopants could be oxygen, carbon or an element specific to the chemistry of the synthesis itself. Thin films prepared in the Chapter 4,5 and 6 show similar electrical properties for example, degenerate p-type conductivity with carrier concentration of $\sim 10^{18} \text{ cm}^{-3}$ and low mobilities in the range $0.1 - 2.12 \text{ cm}^2/\text{V}\cdot\text{s}$. Although the thin films were prepared by different deposition methods, their electrical properties were found to be quite similar. The same is also observed in the recent studies on pyrite thin film.¹⁴ This suggests that the extrinsic impurity may not be playing an

important role in pyrite, but rather the conduction is dominated by other factors. However, the natural crystal studied in this chapter showed Ca impurity in RBS, see Figure 6.16 Chapter 6. Ca impurity might affect the conductivity as well, but given the data in the literature the understanding on its impact is limited. Apart from that microscopic voids and inclusions may also complicate the interpretation of the data.

- (ii) **Phase impurities** – Existence of phase impurities can also affect the conduction mechanism in pyrite. Since the other undesirable Fe-S phases are metallic, their presence in crystalline or amorphous form could be responsible for the conduction behavior observed at low temperatures in Figure 7.8. There is evidence for metal-insulator transition in pyrite due to phase decomposition.¹⁵ If either the bulk or surface decomposes to other Fe-S phase such as Fe_{1-x}S , FeS etc., it might account for the observed phenomena. However, no evidence of phase impurity is found in our crystals from Raman spectra at room temperature, see Figure 7.5. In addition to that, the S ; Fe stoichiometry was also found to be close to 2 discounting this possibility.. However, a phase transformation at low temperatures cannot be ruled out. If a phase transformation occurs selectively at the surface or in the bulk, the inherent resistivity could change dramatically, triggering different current paths in each configuration tested. This could be a very plausible explanation for the phenomenon observed in Figure 7.8. Unfortunately, we could not verify this possibility during the course of this project.
- (iii) **Surface Inversion layer** – Surface inversion in pyrite is recently attributed to high hole carriers which could in turn increase the surface conductivity.^{1,2,9} One of the investigations was based on temperature dependent Hall and conductivity measurements on synthetic crystals. As the temperature was decreased, Hall coefficient changed from negative to

positive at temperature around 100 K – 150 K along with the change in conductivity.¹ Similar type of carrier crossover from p-type to n-type is also observed in pyrite thin films.¹⁶ The temperature range at which resistance increases in hybrid configuration is coincidentally similar to the temperature range mentioned above on a synthetic crystal from Law et al.¹ However, we have no direct evidence to establish the presence of surface inversion layer in our experiments. We can only resort to support the literature, see Figure 2.6 Chapter 2 and also for the films prepared Chapter 4, 5 and 6. Thin films have shown to exhibit p-type conductivity while crystal showed n-type behavior with higher mobility than the thin films. It is intuitive from simple geometric considerations that polycrystalline thin films would have a lot of grain boundaries unlike in single crystals. So the surface effects would dominate more in the case of thin film than in the bulk crystal. This can be correlated to the n-type and p-type behavior of the crystal and the bulk respectively. This is perhaps the reason why photoelectrochemical cells and Schottky barrier cells have been reported from single crystals while no photoactivity is exhibited by thin films. Careful further study is required before claiming the presence of surface inversion at room temperature.

- (iv) **Measurement Artifacts** – Since such type of measurement is done for the first time on pyrite single crystals, there are possible sources of errors as well. The analysis is based completely on measuring resistance as a function of temperature. It is noteworthy that the as the temperature is decreased, other material parameters might also change, for example resistivity. Change in the resistivity will also affect the resistance. If the resistivity dependence on temperature is different between the surface and the bulk due to differences in Fe and S coordination, there could be a change in current path as the temperature is decreased. This could be misinterpreted as surface inversion.

7.4 Conclusions

- The natural iron pyrite cubic specific used in this study was proven to be a single crystal, oriented along [100] directions, phase pure and stoichiometric.
- The crystal was shown to be n-type with carrier concentration of around 10^{16} cm^{-3} and Hall mobility of $64 \text{ cm}^2/\text{V-s}$.
- An experiment to measure electrical transport was designed and successfully used to prove a significant difference between bulk and surface resistances at temperatures $< 120 \text{ K}$.
- Temperature dependence of resistance of the device in different configurations proved the surface to be more conducting than the bulk at temperatures $< 120 \text{ K}$.
- At temperatures near the room temperature no difference could be detected between bulk and surface resistivities.
- The results indicate that the surface and bulk resistances differ significantly in pyrite at low temperatures. The reason for this phenomenon is unclear. Along with many possibilities discussed such as extrinsic dopants, phase impurities and measurement artifacts, surface inversion layer may be additionally responsible for the difference in resistance.

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Chapter 8

Concluding Summary and Future Work

This chapter summarizes the results obtained from iron pyrite thin films prepared by various techniques, namely spray pyrolysis of Fe and S precursors, hot-injection chemical synthesis of nanocubes from FeCl_3 and elemental S precursors followed by spin coating and pulsed laser deposition from synthetic targets and a natural single crystal target. The films were extensively characterized for structural, optical and electrical properties to understand the reasons for their poor photovoltage generation in solar devices despite the beneficial band gap and optical absorption coefficient of bulk pyrite. The different techniques used to fabricate the material and the film permitted generation of an effective platform to compare films with different defect characteristics, and assess the role of these defects in influencing the optoelectronic properties. This thesis documents a crucial body of knowledge and information which could explain many unusual behaviors reported in pyrite thin films, and even dispel some inaccurate hypotheses to explain the experimental data. Future projects are suggested based on the results and insights provided in this work.

The pyrite thin films investigated here could be compared with those reported in the literature in a convenient, overarching manner in a plot of Hall Mobility against Carrier Concentration which is shown Figure 8.1. This figure is identical to Figure 2.6 given in Chapter 2 to map the films used by researchers in other works, except that the information obtained in this study are included as red data points. Red triangle ($\blacktriangle$) is for the natural single crystal studied in this project; the red circles are for spray pyrolyzed and PLD fabricated and sulfur heat treated iron pyrite thin film; the red square is for spin coated and sulfur heat treated nanocube thin film. It is clear that our data on pyrite films and single crystal map very well within the regions for films (purple) and single crystals (yellow) of previously reported studies on pyrite.

Figure 8.1 Hall mobility vs carrier concentration of pyrite crystals thin films and nanostructures. Additional red points in the graph represent pyrite studied in this work (refer Figure 2.6).

8.1 Contribution and Summary of the Work

8.1.1 Spray Pyrolyzed Thin Films

Spray pyrolysis of Fe and S precursors produces amorphous films. Sulfurization treatment of the amorphous films is necessary and the effective sulfurization parameters are: temperature range of 400° C – 500° C and the time of 30 mins to

achieve good crystallinity and single phase pyrite films. An optical band gap of 1.04 eV was measured but it fits with the direct band gap relationship. Surface sensitive measurements (UPS) prove that the surface is prone to defects such as Fe_{1-x}S while the in-depth RBS data gives S: Fe ratio of 2:1. Hall and Seebeck analyses revealed p-type behavior with high hole concentration of $\sim 10^{18} \text{ cm}^{-3}$ and mobility of $2.12 \text{ cm}^2/\text{V-s}$. Absence of Schottky barrier, and temperature dependent Seebeck and electrical measurement showed the behavior to be that of a degenerate semiconductor with small thermal activation energy of 39 meV. Observation of Mott-variable range hopping (VRH) from temperature dependence of resistance supports the existence of localized gap states. Moreover, decreasing the temperature below 50 K leads to crossover from Mott-VRH to ES-VRH transport due to non-negligible coulomb interaction. This indicates that electronic disorder in the material is responsible for degenerate conduction and also explains why optical transition in pyrite fits with direct band instead of indirect band gap.

These films proved to be excellent catalysts in Dye Sensitized Solar Cells (DSSC) when used as a counter electrode in place of platinum and PEDOT. These films drove the I_3^-/I^- and $\text{Co(III)}/\text{Co(II)}$ redox reactions in the dye sensitized solar cell very efficiently. Further, photon energy conversion advantage was derived by lower charge transfer resistance, higher surface roughness and increased light reflection from the pyrite counter electrode. The overall performance of the DSSC with pyrite counter electrode was found to be equally good to the state-of-the-art catalyst for the particular redox couple (Pt and PEDOT) DSSC

8.1.2 Spin Coating of Nanocubes for Thin Films

(100) faceted iron pyrite nanocubes of size $\sim 100 \text{ nm}$ were synthesized by the hot-injection method and then spin coated to fabricate thin films. Sulfurization treatment at 500°C for 1 hour helps in removing the surface insulating ligands

used in the synthesis process, and improving the electrical conductivity of the film while retaining the cubic shape of the pyrite nanoparticles. This film was different to the spray pyrolyzed films in that the film contained a collection of single crystal nanocubes but with good electrical contact between them.

Hall measurements showed p-type behavior with carrier concentration of $\sim 10^{18} \text{ cm}^{-3}$ and mobility of $0.10 \text{ cm}^2/\text{V}\cdot\text{s}$. Ultrafast laser pump probe spectroscopy provided greater insights into the charge carrier dynamics and carrier loss mechanisms in this film. Two carrier transient decay components were detected; one fast, of the order of picoseconds, and another slow, of the order of nanoseconds. The fast component has a characteristic decay time constant of $\tau_F \sim 1.8 \text{ ps}$ which could be attributed to carrier localization to indirect and shallow defect energy bands. The slow component has a characteristic decay time constant of $\tau_S \sim 990 \text{ ns}$ which could be attributed to deep defect level relaxation and recombination via hole capture process. These relaxation processes to defect levels within the prohibited band gap leads to significant voltage loss in photo voltage generated by photon absorption in a solar device. Such study on charge carrier dynamics to probe carrier lifetimes and relate them to photo voltage losses in pyrite has been done in this study for the first time, to the best of our knowledge.

Temperature dependent electrical measurements showed degenerate semiconducting behavior with an activation energy of 87 meV . The presence of localized defect states elucidated by the optical pump-probe technique manifest themselves in pyrite by a hopping charge transport mechanism which could be described by the Mott-VRH transport model.

The magnetic behavior of the film was diamagnetic at room temperature, as expected. However, at very low temperatures ($\sim 10 \text{ K}$) a weak magnetic ordering was detected. This is again a possible consequence of defects such as S vacancies forming low energy configuration which might be leading to localized S deficient

phases such as $\text{FeS}_{2-\delta}$ ($0 \leq \delta \leq 1$) which have a magnetic ordering.

On the basis of quantitative analysis of defect states, a defect model is proposed in this thesis to explain the photocarrier loss mechanisms that could be operating in pyrite.

An infrared sensitive photodiode was made with pyrite nanocubes to prove the practical applicability of such solution processed and spincoated films in PV related devices.

Heterojunction solar cells made from these nanocube films showed a photovoltage of around 100 mV, which is higher than any reported in the literature for pyrite nanoparticle based solar cells.

8.1.3 Pulsed Laser Deposited Pyrite Thin Films

Iron pyrite thin films were successfully fabricated by Pulsed Laser Deposition using synthetic and natural single crystal targets. Prior to this work, there had not been any attempts to use PLD to produce pyrite thin films. Subsequent sulfurization treatment is required to convert the amorphous, as-deposited films to crystalline, single phase films. The films prepared in this manner however showed no photoactivity. They were found to have p-type conductivity with a degenerate semiconductor behavior as other films studied in this project.

Two different sulfurization treatments were investigated for the films deposited using natural single crystals. They were thermal sulfurization plasma sulfurization using H_2S gas. The plasma sulfurized sample contained evidence of marcasite impurity while the thermally sulfurized sample was pure pyrite. Both these films did not show any photoactivity and showed degenerate p-type conduction behavior with an activation energy of 49 meV. Marcasite phase

containing film showed slightly higher conductivity than phase pure film. Temperature dependence of resistance showed Mott-VRH transport mechanism to be operative over a wide temperature range of 60 K – 250 K, again highlighting the role of defects in the film. Thus, pyrite films contain enough disorder and defects that severely limit their application in photovoltaic devices. The presence of some impurity marcasite phase did not seem to have any significant effects on the electrical conduction properties and hence, the poor photo voltage generated by pyrite films cannot be attributed to impurity phases.

8.1.4 Experiments on Natural Pyrite Single Crystal

Natural pyrite single crystal was characterized for structure and phase purity. S: Fe elemental ratio of the crystal was determined to be 2. An attempt was made to deconvolute the surface and bulk resistances by designing a special electrical experiment. Some interesting phenomena were observed in this experiment as the temperature was decreased. The surface resistance was found to increase substantially over the bulk resistance for temperatures < 120 K. This finding seems to support the existence of a Surface Inversion layer in pyrite crystals at low temperatures. This was hypothesized by researchers previously.

8.1.5 Sulfurization Process: Thermodynamics vs Kinetics

After analyzing the films obtained in Chapter 4, 5 and 6, it was evident that high temperature sulfurization process is important to achieve good crystallinity and phase purity. However, nanocubes synthesized by hot-injection method showed high crystallinity even at low temperature and subsequent sulfurization was done only to ensure a good electrical conductivity. This suggests that hot-injection method is a quasi-equilibrium process and instead of thermal diffusion, kinetic factors dominate the crystal growth through oriented attachment (OA) and LaMer process. As a result, this method provides advantage over conventional equilibrium methods which require high temperature for phase formation. However, for other films, sulfurization process was

required to obtain the equilibrium phase and the choice of sulfurization temperature was guided by the Fe-S phase diagram. The final sulfurization temperatures of the relevant films were experimentally verified. In such diffusion limited sulfurization equilibrium processes, sulfur diffusion in the Fe-S system determines the phase formation and grain growth. However, it should be noted that the sulfur diffusivity is limited in the intermediate Fe-S compounds and can potentially suppress the kinetics which may in turn influence the equilibrium of phase formation.

8.2 Overall Conclusions

- Iron pyrite thin films were prepared by spray pyrolysis, spin coating of hot-injection synthesized nanocubes and pulsed laser deposition from targets of pyrite natural crystal and synthetic pellets. Sulfurization process plays pivotal role in obtaining crystalline and phase pure pyrite films. H₂S plasma sulfurization of some PLD deposited films showed definite signs of marcasite impurity.
- Spray pyrolyzed and PLD deposited films showed no photoactivity while spin coated nanocubes showed photoresponse with slow rise and decay time of photocurrent current when the light was on and off respectively.
- Ultrafast laser spectroscopy was deployed for the first time to study carrier dynamics of pyrite. Photoactive pyrite nanocubes showed two dominant relaxation mechanisms. Fast localization from higher energy states to band edge with lifetime of $\tau_{ct} \sim 1.8$ ps and slow relaxation through deep midgap states with longer lifetime $\tau_r \sim 990$ ns. These relaxation processes to intermediate states are responsible for the low photovoltage.
- Optical absorption for the films produced by different methods showed absorption below the band gap. Optical bandgap of the films was found to be direct gaps at energies of 1.04, 1.02 and 1.01 eV for spray pyrolyzed, spin-

coated nanocubes and PLD films respectively. Mixed phase film of pyrite and marcasite also showed a band gap of around 1.05 eV. Direct gap behavior observed for all three types of films suggest that films contain high defect densities regardless of the growth technique. Thus, the intrinsic disorder in the pyrite itself seems to dominate its optical behavior.

- Similar electrical behavior was observed for pyrite films prepared by spray pyrolysis, spin-coating of nanocubes and PLD. All three types of film showed p-type behavior with carrier concentration of $\sim 10^{18} \text{ cm}^{-3}$ and mobilities of 2.12, 0.10 and 1.4 $\text{cm}^2/\text{V-s}$ respectively. This again indicates that the electrical properties are dominated by intrinsic factors.
- Temperature dependent electrical measurements showed Mott-VRH transport for pyrite films synthesized by the three different methods
 - For spray pyrolyzed film, 65 K – 255 K marks the temperature regime of Mott-VRH transport.
 - For nanocube film, 70 K – 250 K marks the temperature regime of Mott-VRH transport.
 - For PLD film, 60 K – 250 K temperature range is identified for Mott-VRH transport.

Since Mott-VRH is a characteristic of the carrier transport mechanism via localized defect states, Mott-VRH transport for all three films indicates the existence of intrinsic disorder in the pyrite thin films. So the intrinsic defects in pyrite are severe enough to cause an impact on electronic and transport properties of the material. Achievement of pure phase films does not guarantee good optoelectronic behavior in pyrite, as indicated in the literature.

- Electrical transport measurement method was adapted from the literature on topological insulator and applied to our pyrite single crystal to study the bulk and surface resistivities for the first time. Pyrite natural crystal showed difference in the bulk and surface resistivities at low temperature. No difference in bulk and surface resistivities was found at room temperature.
- Spray pyrolyzed films were used as counter electrodes in DSSC demonstrating efficiencies (η) of 8.0 % and 6.3 % with iodine/iodide redox and Co(III)/Co(II) redox electrolyte respectively. These efficiencies compete with state of the art catalyst Pt for iodine/iodide ($\eta = 7.5$ %) and PEDOT for Co(III)/Co(II) ($\eta = 6.3$ %) redox electrolyte DSSCs respectively.
- Heterojunction solar cells made from pyrite nanocubes with CdS yield photovoltage of around 100 mV, which is the highest for pyrite based solar cell.

8.3 Future Work and Possible Directions

Electrical transport measurements of spray pyrolyzed and sulfurized thin film shows the Mott-VRH to ES-VRH. This result is an interesting one and should be further studied. Magnetoresistance measurements would be very insightful and provide further information regarding localization lengths and disorder. Aspects of metal-insulator transition (MIT) can be anticipated as the disorder is increased.

Electrical transport measurements of sulfurized nanocubes thin films show unusual resistivity saturation at low temperature (below 50 K). This is an extremely important subject for nanocrystalline thin film transport. Low temperature transport must be focused in detail in context of fluctuation induced tunneling (FIT) conduction and metallic transport.

High quality pyrite nanocubes thin film shows photoactivity, which reinforces the need of high quality single crystalline thin films for better photoactivity. Thus epitaxial growth of pyrite single crystal thin films is required by PLD, MBE or ALD. Extension of the current PLD work must be in the direction of growing epitaxial single crystal thin films.

Electrical measurement designed and discussed in the work to probe surface conduction of natural pyrite single crystal must be performed for synthetic single crystals of pyrite. Also, the technique applied in the work should be adopted for other semiconductors with surface accumulation or inversion layer problem. To suppress the conducting surface layer of pyrite, ion implantation could be beneficial. Control ion dosage and range of desired implanted ion species could potentially change the surface carrier type. Based on the work on chalcogenide surface charge carrier type reversal, Bi ion implantation could be a useful choice.

APPENDIX A

Sulfur quantity calculation for sealing in the ampoule

Figure A.1 Schematic of the quartz tube dimension and notation of the parameters.

- Pressure inside the ampoule will be dictated by the volume inside and sulfur vapour pressure.
- Ampoule is imagined as a cylinder minus the curved area.
- Sulfur vapour pressure is a function of temperature. at a given temperature, quantity the sulfur can be computed to safe pressure limits that ampoule can tolerate (we choose 2 atm).

Calculation steps:

Step 1. Take the inner radius and calculate Volume using

$$V = \pi R^2 h \dots\dots\dots (1)$$

Then plug this in ideal gas equation to calculate number of moles

Step 2. Calculate n from the equation $PV = nRT \dots\dots\dots (2)$

Choose $P = 2 \text{ atm}$ for safety. T in Kelvin, $R = 82.05745 \text{ cm}^3 \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$

Step 3. Convert moles to grams ($M = n * \text{molar mass of sulfur (32.065 gm/moles)}$)

Example calculation: $h = 15$ cm (excluding curved region)

Inner diameter = 1.1 cm, so $R = 0.55$ cm

From equation (1), $V = 14.26$ cm³

Now, $= nRT$, taking sulfurization temperature $T = 450^\circ\text{C}$ (723 K) and $R = 82.05745$ cm³.atm.K⁻¹.mol⁻¹ and for safety, take $P = 2$ atm,

$n = 0.0004807$ mol $\rightarrow 0.01541$ gm = 15.41 mg

Important Notes:

- (1) While putting the sulfur inside the ampoule, sulfur should not stick to the opening or walls of the tube as flame might come in to contact of sulfur directly
- (2) If the film already contains sulfur, then it is better to use even lesser amount of sulfur powder in the ampoule
- (3) Always refer to the sulfur vapor pressure curve whenever you perform a new calculation or recipe

APPENDIX B

I-V Data for the Natural Crystal Transport Measurements

Temperature	Top configuration	Bottom configuration	Hybrid configuration
30	9.92×10^{-5}	0.0016	0.206
40	9.24×10^{-4}	0.0011	0.023
50	0.001	6.93×10^{-4}	0.027
60	0.001	3.02×10^{-4}	0.028
70	9.29×10^{-4}	8.92×10^{-5}	0.027
80	6.90×10^{-4}	3.63×10^{-6}	0.023
90	4.79×10^{-4}	2.67×10^{-5}	0.017
100	3.12×10^{-4}	3.89×10^{-5}	0.011
110	1.94×10^{-4}	6.89×10^{-5}	0.005
120	1.05×10^{-4}	1.15×10^{-4}	0.002
130	5.04×10^{-5}	1.48×10^{-4}	5.14×10^{-4}
140	1.48×10^{-5}	1.72×10^{-4}	8.94×10^{-5}
150	4.44×10^{-6}	1.80×10^{-4}	5.06×10^{-5}
160	1.34×10^{-5}	1.56×10^{-4}	5.90×10^{-5}
170	1.63×10^{-5}	1.20×10^{-4}	5.71×10^{-5}
180	1.19×10^{-5}	6.54×10^{-5}	4.91×10^{-5}
190	1.07×10^{-5}	9.53×10^{-6}	3.46×10^{-5}
200	5.64×10^{-6}	1.46×10^{-5}	1.34×10^{-6}
210	4.23×10^{-6}	1.44×10^{-5}	1.11×10^{-7}
220	6.92×10^{-7}	9.05×10^{-6}	1.04×10^{-5}

230	6.82×10^{-6}	4.43×10^{-6}	2.43×10^{-5}
240	1.50×10^{-5}	2.13×10^{-7}	3.18×10^{-5}
250	2.23×10^{-5}	9.53×10^{-6}	3.98×10^{-5}
260	3.10×10^{-5}	1.93×10^{-5}	5.06×10^{-5}
270	3.68×10^{-5}	3.36×10^{-5}	5.49×10^{-5}
280	4.17×10^{-5}	4.64×10^{-5}	6.34×10^{-5}
290	5.05×10^{-5}	5.82×10^{-5}	6.89×10^{-5}
300	5.77×10^{-5}	7.10×10^{-5}	7.48×10^{-5}
310	6.12×10^{-5}	8.73×10^{-5}	8.04×10^{-5}
320	6.56×10^{-5}	1.02×10^{-4}	8.60×10^{-5}
330	6.62×10^{-5}	1.13×10^{-4}	9.16×10^{-5}
340	7.04×10^{-5}	1.24×10^{-4}	9.63×10^{-5}

List of Publications

1. S. Shukla, N.H. Loc, P.P. Boix, T.M. Koh, R.R. Prabhakar, H.K. Mulmudi, J.Zhang, S.Chen, C.F.Ng, C.H.A.Huan, N. Mathews, T. Sritharan, Q. Xiong. “Iron Pyrite Thin Film Counter Electrodes for Dye-Sensitized Solar Cells: High Efficiency for Iodine and Cobalt Redox Electrolyte Cells”, *ACS Nano*, **2014**, 8(10), 10597.
2. Z. Yang, M. Wang, S. Shukla, Y. Zhu, J. Deng, H. Ge, X. Wang, Q. Xiong. “Developing Seedless Growth of ZnO Micro/Nanowire Arrays towards ZnO/FeS₂/CuI P-I-N Photodiode Application”, *Sci. Rep.*, **2015**, 5, 11377, 2015.
3. S. Shukla, G. Xing, H. Ge, R.R. Prabhakar, S. Mathew, S. Zhenghua, V. Nalla, T. Venkatesan, N. Mathews, T. Sritharan, T.C. Sum, Q. Xiong. “Origin of Photocarrier Losses in Iron Pyrite (FeS₂) Nanocubes”, **2016**, *ACS Nano*, 10(4), 4431.
4. R.A. Abraham, A.C. Nguyen, Y. Chen, S. Shukla, S. Chen, N. Mathews. Modulating Cationic Ratios for High Performance Transparent Solution-Processed Electronics. *ACS Applied Materials & Interfaces*, **2016**, 8(2), 1139.
5. R.R. Prabhakar, S. Zhenghua, Z. Xing, S. Shukla, T. Baïke, L.H. Wong. “Photovoltaic Effect in Earth Abundant Solution Processed Cu₂MnSnS₄ and Cu₂MnSn(S, Se)₄ Thin Films”, *Solar Energy Materials and Solar Cells*, **2016**, 157, 867.
6. R.A. Abraham, A.C. Nguyen, S. Shukla, N. Tiwari, C. Shi, N.G. Ing, N. Mathews. Low Temperature Chemical Transformations for High-Performance Solution-Processed Oxide Transistors”, *Chemistry of Materials*, **2016**, 28, 8305.

8. A. Guchhait, S. Zhenghua, Y.F. Tay, S. Shukla, W. Li, S.W. Leow, J.M.R. Tan, O. Gunawan, L.H. Wong. "Enhancement of Open-Circuit Voltage of Solution-Processed $\text{Cu}_2\text{ZnSnS}_4$ Solar Cells with 7.2% Efficiency by Incorporation of Silver", *ACS Energy Letters*, **2016**, 1, 1256.
9. A. Prakash, P. Xu, A. Faghaninia, S. Shukla, J.W. Ager, C.S. Lo, B. Jalan. "Wide Bandgap BaSnO_3 Films with Room Temperature Conductivity Exceeding 10^4 Scm^{-1} ", *Nature Communications*, **2017**, *Accepted*.
10. S. Shukla, S. Mathew, H.S. Choe, Y. Liu, T. Venkatesan, W. Junqiao, W. Walukiewicz, T. Sritharan, J.W. Ager. "Disorder Induced Variable Range Hopping in Iron Pyrite Thin Films", **2017**, *In Preparation*.
11. S. Shukla, H.S. Choe, Y. Liu, J. Beeman, W. Junqiao, T. Sritharan, J.W. Ager. "Temperature Dependent Resistance Anisotropy in Bulk and Surface Charge Transport of Natural Single Crystal Iron Pyrite", **2017**, *In Preparation*.

Conference Presentations

1. S. Shukla, J.W. Ager, Q. Xiong, T. Sritharan. On the origin of photocarrier losses in Iron pyrite nanocubes: Charge carrier dynamics and electrical transport study, 43rd IEEE Photovoltaic Specialist Conference (PVSC), Portland, USA, 2016. (Full paper)
2. S. Shukla, Q. Xiong, T. Sritharan. Iron Pyrite for Solar Energy Harvesting. EUPVSEC 2015, Hamburg, Germany, September, 2015.
3. S. Shukla, N. Mathews, Q. Xiong, T. Sritharan. Iron pyrite for solar energy harvesting: from potential and problems to application. ICMAT and IUMRS-ICA, Singapore, June, 2015.