Fabrication and Characterization of Antimony (Sb) doped Zinc Phthalocyanine (ZnPc) Thin Films

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289-FET/MSEE/F12

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This dissertation is submitted to Faculty of Engineering and Technology, International Islamic University Islamabad Pakistan for partial fulfillment of the degree of **MS Electronic Engineering** with specialization in **Renewable Energy** at the Department of Electrical Engineering.

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Certificate of Approval

This is to certify that the work contained in this thesis entitled, **"Fabrication and Characterization of Antimony (Sb) doped Zinc Phthalocyanine (ZnPc) Thin Films"** was carried out by **Mr. Muhammad Ibraheem, Registration No. 289-FET/MSEE/F12** and it is fully adequate in scope and quality for the degree of MS Electronic Engineering.

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Declaration

I certify that research work titled **"Fabrication and Characterization of Antimony (Sb) doped Zinc Phthalocyanine (ZnPc) Thin Films"** is my own work and has not been presented elsewhere for assessment. Moreover, the material taken from other sources has also been acknowledged properly.

Muhammad Ibraheem

289-FET/MSEE/F12

Date: 25/08/2017

بِسْمِ اللّٰهِ الرَّحْمٰنِ الرَّحِيْمِ

In the name of Allah (SWT), the most beneficent and the most merciful

Dedicated

to

my **parents** who have always supported me morally and financially, and have always prayed to Almighty ALLAH for my success, to my entire family members and to my respected teachers.

Acknowledgement

Glory be to **Allah** and praise be to Him equivalent to the number of His creation and equivalent to what pleases His Beings and equivalent to the weight of His throne and equivalent to the ink of His words. Peace and blessing of Allah be upon His last **Prophet Muhammad (Peace be upon him)** and all his **Sahaba (Razi-Allaho-Anhum)** who devoted their lives for the prosperity and spread of Islam.

I would like to say heartiest thanks to my Supervisor **Dr. Afzal Hussain Kamboh** and Co-Supervisor **Dr. Saeed Badshah**. I pray from the deepest core of my heart that Almighty ALLAH give them long life, good health and courage to serve this country and the whole humanity,(Amin).

I am deeply grateful to my senior **Muhammad Imran** for his unconditional backing and suggestion during my investigation of this thesis work in laboratory and further write up stages. I adore the lab environment where I completed this work due to welcoming and amiable attitude of lab fellows that made my work for easier than I thought. I would like take this opportunity to thank my lab Assistant **Mr. Khalid Jan Afridi** and **Mr. Zulkaif** for their help and cooperation during my research work.

Abstract

Zinc phthalocyanine (ZnPc) is a promising candidate for solar-cell applications, because it is easily synthesized and is non-toxic to the environment. In the visible region of the electromagnetic spectrum, antimony(Sb) doped zinc phthalocyanine(ZnPc) thin films exhibits a good absorption, it can be very useful in the devices for the conversion of solar energy.

Zinc phthalocyanine (ZnPc) were deposited on Indium tin oxide (ITO) coated glass after doping with Antimony (Sb) through Physical Vapor Deposition (PVD) technique (heat resistive high vacuum evaporation). The Sb doping percentage was confirmed by Energy Dispersive X-ray spectroscopy (EDX) then different characterizations were carried out including, electrical characterization for I-V curves, optical characterization by UV-VIS transmission spectroscopy and Morphological analysis.

With the increase in antimony contents from 0% to 3.27% as verified by EDX, increase in current from 1.85×10^{-6}A to 4.85×10^{-3}A at 2.80×10^{-1}V has been studied by I-V results which show the increase in conductivity. Schottky type diode was found. The band gap was decreased (from 1.86ev-1.58ev) and absorbance range increased (from 140nm to 240nm) as shown through optical characterization.

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Chapter 1

Introduction

For more than a century, semiconductors have been known and experimented by the people, and are being used throughout that time. However, the real impact of semiconductors on our lives was really fully realized during the beginning of the Information Age. Desktop PCs, laptops, home appliances, smart phones and all of the other things that make life so easy these days are all dependent upon semiconductor technology. Without semiconductors, the life would resemble the Industrial Age, when the amazing technology was light bulbs in the world.

One of the important technologies where semiconductors are being used now is the technology of conversion of solar energy into electricity. As we know that the demand of energy in the world is going on higher side with the increase of the population. We also know that fossil fuels are the major energy source in the world today. But some serious environmental problems like air pollution etc are linked with the energy production from fossil fuels. Carbon monoxide, sulphur dioxide, nitrogen dioxide, Carbon dioxide etc. are some of the gases that are released by fossil fuels that can have severe consequences on the habitats. These fossil fuels once are utilized, it won't be available. There are limited sources and they are depleting very fast.

The solution of the above problems is renewable energy for which a lot of research work has been conducted and much more is required. One of the important sources of renewable energy is the solar energy. Solar energy is a sustainable resource for energy consumption and for an indefinite period it is renewable. The history of solar power is very old; after the photovoltaic effect observation of Alexandre Edmond Becquerel via an electrode in a conductive solution exposed to light. Since the first deput of solar technology in 1954, it has evolved a lot. At that time, a silicon solar cell with 4

percent efficiency was first produced by Bell Telephone Laboratories. Since then researchers have been working for improving the efficiency and to decrease the cost. Hundreds and thousands of solar cells make a solar PV array that converts sunlight into electricity. More efficiency has been achieved but there is a need of new technology to boost this light capture and conversion with much more efficiency.

Photovoltaic (PV) technologies for solar energy conversion represent promising routes to green and renewable energy generation. Despite relevant PV technologies being available for more than half a century, the production of solar energy remains costly, largely owing to low power conversion efficiencies of solar cells. The main difficulty in improving the efficiency of PV energy conversion lies in the spectral mismatch between the energy distribution of photons in the incident solar spectrum and the bandgap of a semiconductor material[1].

Photovoltaic cells fabricated with organic semiconductors have attracted considerable attention because of their flexibility in varying their electrical and optical properties, and in general they can be more easily fabricated than any inorganic photovoltaic cells. Also organic semiconductors are promising materials for other optoelectronic applications such as light-emitting diodes (LEDs) and optical switches [2].

Organic materials have potential advantages for use as active layers in electroluminescent displays as well as photoelectric and sensor devices, because they are easily process able in low cost and large area device fabrication [3].

1.1 Semiconductors

Semiconductors are being used everywhere. The computers are controlled by semiconductors to study and to conduct businesses also the communication devices such as phones and mobiles, the transport like cars and planes, the hospital

equipments used to diagnose disease, the systems used by military for protection of the people, and the gadgets for entertainment such as iPods, TVs and Videogames. These latest developed technologies are not possible without semiconductors.

Usually semiconductor is a solid material which conducts electricity under particular conditions. The electric conductivity takes place between conductor and insulator. The conductivity of a semiconductor is somewhat directly proportional to the temperature that is, increases with increasing temperature. This act is quite contradictory to a metal. One of the main properties of semiconductors is effective magnitude of environment specifically passing current in one direction is more smooth and fluent than the other. As the conductive behavior of a semiconductor can be altered by the regulating the increasing amount of impurities or by electrical fields utilization or changing the brightness, semiconductors are very practical instruments for signals magnification, switching, and energy preservation.

In a semiconductor the flow of current takes place by free electrons and "holes", conjointly admitted as charge carriers. Impure atoms or impurities can be accumulated to a semiconducting material, the process known as "doping", and the resulted in raise of the number of charge carriers incredibly inside it. Semiconductor can be either a p-type or n-type depending on the doped semiconductor, if it comprises of surplus holes it is known as "p-type", and when it consists of plenty of free electrons it is known as "n-type". The position and concentration of p- and n-type dopants can be checked accurately in the doped semiconductor in any instruments as the doped semiconductor used, is prepared under greatly regulated environment. Various p- and n-type areas can be found in a single semiconductor crystal; the p-n junctions between these fields have abundant functional electronic characteristics.

The main features relating to a PN junction are its Depletion width, Barrier potential, donor concentration, electric field, ideality factor, etc. These factors differentiate one type of diode from other. Among other one type of these diodes is metal semiconductor junction, which is also commonly admitted as Schottky diode or Schottky barrier.

1.2 Schottky diode

A German physicist Walter H. Schottky invented Schottky diode also known as hot carrier diode, the diode is therefore named after him. The Schottky diode,basically has a very small progressive voltage drop and a very rapid switching activity. The cat's whisker detectors are known as the original basic Schottky diode that was employed in the early power applications in the beginning days of wireless and metal rectifiers.

A very limited voltage drop occurs across its terminals, when forward current passes over a solid-state diode. A conventional voltage drop of 0.6–0.7 V in silicon diode happens, whereas a voltage drop of 0.15–0.45 V happens in Schottky diode. Due to this particular property of the lower voltage drop, a Schottky diode can be used to give rapid switching speeds and better structural efficiency.

Between a metal and a semiconductor, there is a junction establish called a metal semiconductor, developing a Schottky barrier as compared to the original conventional diodes where there is semiconductor–semiconductor junction formation takes place. Molybdenum, platinum, chromium or tungsten, and certain silicides particularly palladium silicide and platinum silicide, are the conventional metals employed, while the n-type silicon semiconductor is common. In this case metal would able to show the anode property while the cathode will be n-type

semiconductor of the diode. This Schottky barrier produced in both very rapid switching and low forward voltage drop.

It is possible to design a junction having properties similar to those of a PN Junction by bonding Al to suitably doped N-type silicon. The junction that results is termed as a metal-semiconductor (MS) Junction. Like a PN junction, the MS Junction express a low resistance to current flow when it is forward biased and a high resistance when reverse biased. A depletion region and a barrier potential are settled in a metal-semiconductor junction by a method identical to that explained for PN junctions, except in this case carrier diffusion consists only of electrons diffusing from the semiconductor to the metal. The electrons concentrate at the metal surface and the depletion region obtained only in the semiconductor side of the junctions.

Metal-semiconductor junctions are able to behave more rapidly than their PN counterparts because only majority carriers (electrons in the N-type silicon) are engage in the process. Diodes build and employed this way are called Schottky barrier diodes, or commonly Schottky diodes. A metal-semiconductor junction with Schottky diode properties can also be made by connecting gold (Au) to P-type germanium. This device is called a gold bonded diode and reacts very quickly in switching operations.

1.3 Organic semiconductors

Organic semiconductors are a novel materials class which has recently been investigated in detail due to the very promising applications possibilities. In contrast to the classical inorganic semiconductors, which are usually used in single-crystalline forms, organic semiconductors consisting of either oligomer or polymer chain molecules are typically deposited as thin films on large areas leading to amorphous or polycrystalline structures. Since flexible and transparent substrates can be used,

organic electronics open many new application and integration perspectives. With contributions from chemistry, physics, and engineering, organic semiconductors are an archetype for an interdisciplinary field [4].

1.4 Orbital structure in organic semiconductors

The orbital structure is usually characterized by their well-built bonding i.e. ionic and covalent bonding between atoms in the lattice. Therefore the transportation of charge can effortlessly be taken place through a strong interaction of overlapping atomic orbital in a blocked structure. By the help of double and single bonding we can distinguish the molecular structures of organic semiconductors. Due to the π conjugation, the molecules illustrate their semi conducting categorization. As per valance bond theory the π conjugation is the vacillation of single and double bonds. It is also explained on the basis of Molecular orbital theory which states that the atomic orbital are collective to form the same amount of molecular orbital. When the orbital over and bond is formed energy is gained. In case of σ-bond, the atoms grasp jointly due to the lowly energy of molecular orbital.

Carbon atoms enclose four valence electrons in their atomic orbital; 2s, 2px, 2py and 2pz. These orbitals hybridize in the configuration of a σ- bonds. Whereas the charge density is symmetrically spread in the shape of two band type layers beneath and over the molecular plane as shown in the figures below.

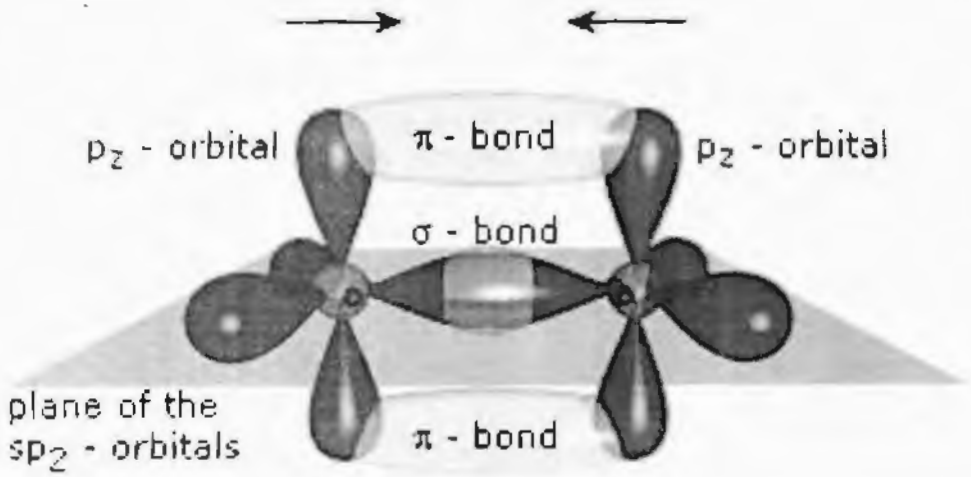

Figure 1.1:Schematic diagram of π- orbital

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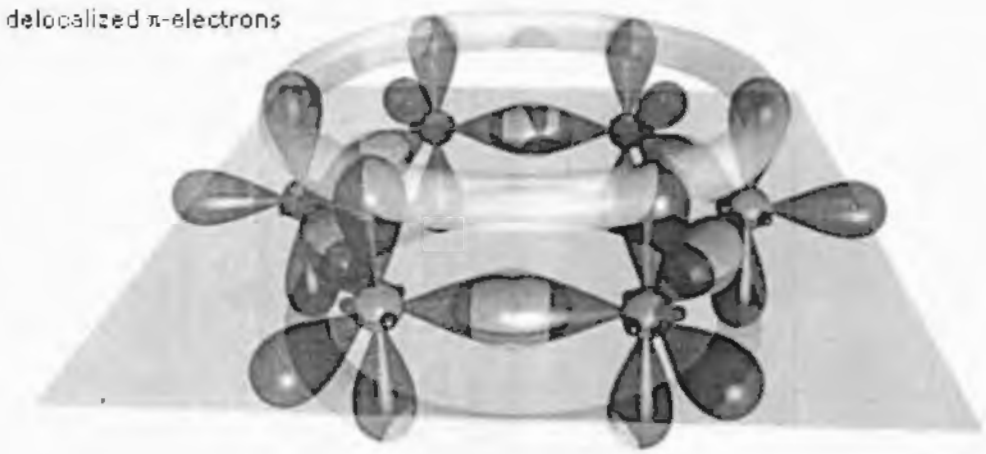

Figure1.2:Delocalization

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Figures 1.1 and 1.2 Schematic diagram of π- orbital symmetrically spread in two band form layers beneath and over the molecular plane and σ-orbitals shaped by hybridization of s, px & py orbitals.

The π- orbitals behaved as delocalized above all the carbon atoms and do not contribute in any type of bonding. These electrons are called mobile electrons or unsaturated electrons because they can freely shift inside the molecule. If both sp2 hybridization and conjugation is accessible in the molecule than these electrons can straightforwardly be transmitted from one position to another as shown in figures below.

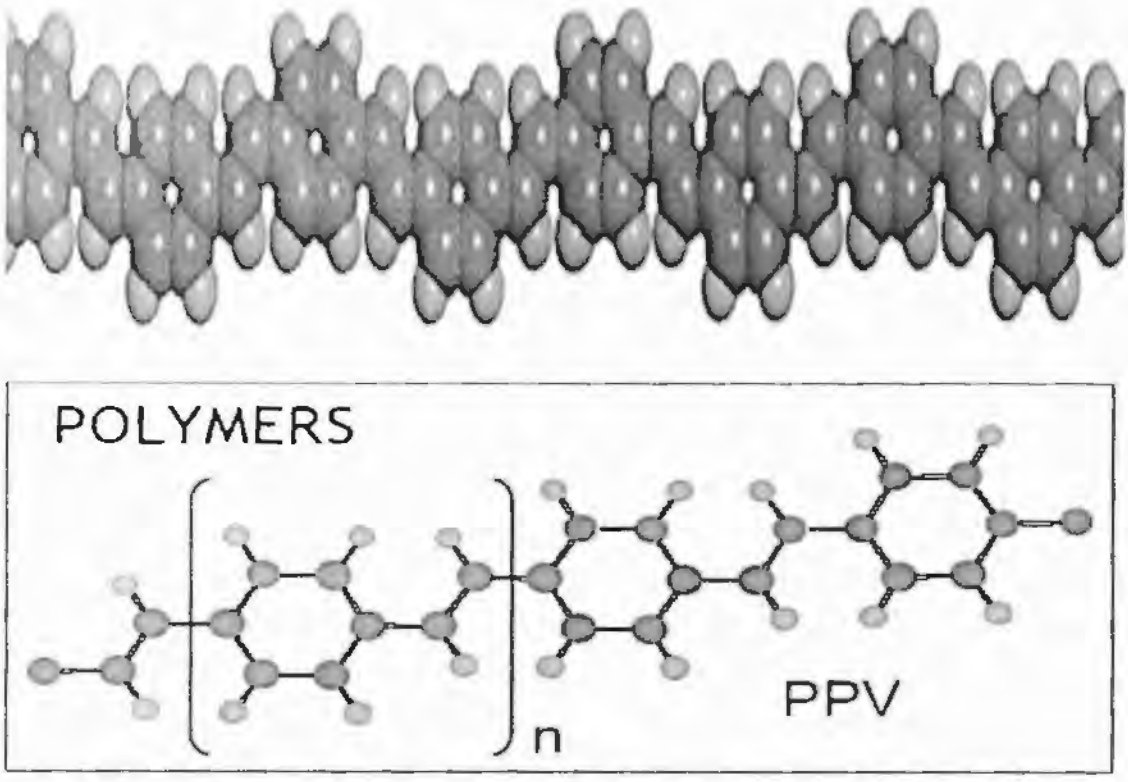

Figure 1.3: Electrical charge transportneeds sp2-hybridization and conjugation in the molecule

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Boundary orbitals may enhanced the electrical properties of molecules i.e. highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO).

Thus in organic materials the HOMO and LUMO are created as an alternative of conduction band and valance band in organic semiconductors as shown in Figure 1.4

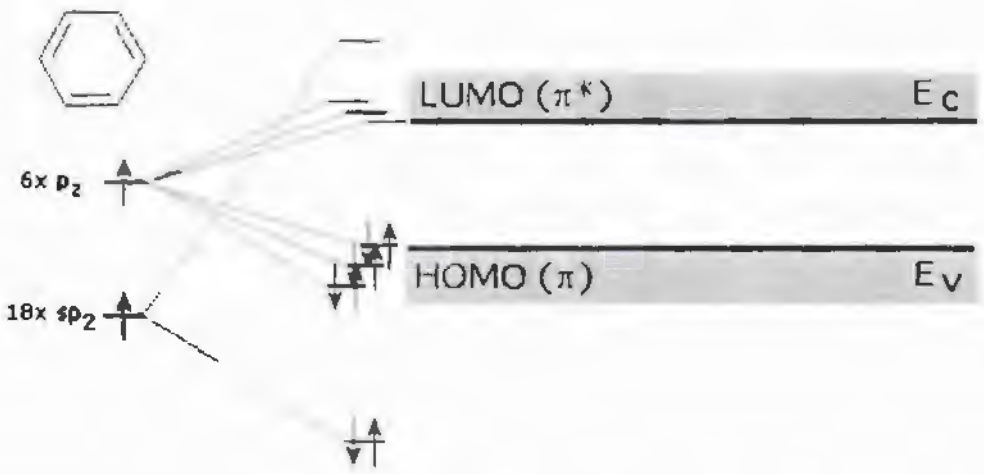

Figure 1.4: HOMO and LUMO

https://www.iapp.de/orgworld.de/images/schema2.png

1.5 Phthalocyanine (Pc)

Organic semiconductors like phthalocyanine have received increasing attention in recent years, particularly as gas detectors and as active components of solar devices. The electrical properties of sandwich structures based on phthalocyanines have attracted most interest to date [5].

Many kinds of phthalocyanines, such as metal-free phthalocyanines and phthalocyanines with various metals have been synthesized and are now utilized in a wide variety of fields like solar cells [4, 6], organic electronics [7], etc.

Phthalocyanine (Pc) compoundshave attracted much attention because they have enormous potential for applications, such as semi conducting devices, photovoltaic and solar cell, gas sensors, and optical recording [8]

1.6 Zinc Phthalocyanine (ZnPc)

Zinc phthalocyanine (ZnPc) is a promising candidate for solar-cell applications, because it is easily synthesized and is non-toxic to the environment. Recently, phthalocyanine (Pc) was considered by many researchers as the active part in all-organic solar cells, i.e. plastic solar cells [5].

Heat treatment of ZnPc samples had great influence on the electrical parameters. The adsorbed oxygen molecules in freshly prepared samples were responsible for lower hole mobility and higher charge carrier concentration. On the other hand, prolonged heating of the ZnPc films at 425 K resulted in lower defect state density, and thus reduced trap concentration and higher charge carrier mobility. Moreover, Passard et al. observed that on oxidation of phthalocyanine molecules the generated excess holes would be hampered from hopping to neighboring neutral molecules and therefore resulting in a lower mobility. This effect is more likely to occur when the dopant concentration is atleast 50% of phthalocyanine molecules are oxidized. It is evident that more work is needed to explain the variation of electrical parameters and

conduction processes with sample preparation conditions, heat treatment conditions and types of electrodes, Ohmic or non-Ohmic contacts.[9]

Thin films of zinc phthalocyanine (ZnPc) is also a good candidate for sensors. Sukhwinder Singh, G.S.S. Saini, S.K. Tripathi investigated ZnPC for sensors.These films have been studied as chemical sensors such as methanol and ammonia[10].

A new zinc phthalocyanine, ZnPc **1**, bearing six bulky *tert*-octylphenoxy groups in peripheral positions, acting as pushing moieties, and an electron-withdrawing carboxyphenyl append, acting as anchoring unit to bind TiO_2 surface, has been synthesized and characterized. ZnPc **1** has been employed as sensitizer in dye sensitized solar cells, showing, in all cases, modest conversion efficiencies without the use of co-adsorbents [11].

One of the well-known organic semiconductors are phthalocyanines which are suitable for use in photovoltaic devices since theirphysical and chemical stability is very high. A number of studies of functional properties of organic semiconductors have recently been carried out concerning both basic and application aspects. Phthalocyanines are one group of such materials, of which optical, electronic and photoelectronic properties are being extensively investigated [12].

For applications of photovoltaic, zinc phthalocyanine (ZnPc) (C32H16N8Zn) is a promising candidate of organic semiconductor.

ZnPc was also used in Ternary organic photovoltaic devices. ZnPc acted as an electron cascade material, providing an efficient energy level offset between the polymeric donor and the fullerence derivative acceptor, enhancing charge transfer,

reducing exciton recombination and thus improving the photovoltaic performance of the devices[13].

ZnPc was also used in the vertical thin film phototransistor and due to the photo-sensitive characteristic of ZnPc, it has a better current amplification effect under illumination[14].

ZnPc can be used in many applications. ZnPc nanocubes can act as potential candidate for electron emitter for field emission display devices and many more [15].

Doping of zinc phthalocyanine (ZnPc) with antimony (Sb) causes in modification of electrical and optical properties of zinc phthalocyanine (ZnPc) including conductivity and resistivity which can better perform in solar cells.

1.7 Problem Statement

For the usage of renewable energy through conversion of solar energy, Photovoltaic is the most suitable candidate in this field. This technology is being used for more than 5 decades but the efficiency of converting the solar energy still requires a lot of improvement. The spectral mismatch between semiconductor's bandgap and incident solar spectrum's energy distribution of photon is one of the most challenging tasks in the research of photovoltaic efficiency improvement.

Also at present low intensity of light environment and higher environmental temperature reduces the efficiency of the material used in photovoltaic cells; therefore to overcome these problems, a modified material is required whose electrical and optical properties should be enhanced for efficiency improvement.

In the visible region of the electromagnetic spectrum, antimony(Sb) doped zinc phthalocyanine(ZnPc) thin films exhibits a good absorption, it can be very useful in the devices for the conversion of solar energy. The electrical properties and the optical properties such as bandgap of zinc phthalocyanine (ZnPc) can be modified with the help of antimony (Sb) doping to a level where the absorption of light is maximum which can result in the improvement of solar cell efficiency.

1.8 Proposed Solution

The main objective is the introduction of a modified organic semiconductor doped with a material. Also it includes the study of the trend of optical band gaps energy and the electrical properties and CV characteristics for different concentration of Antimony (Sb) doped with zinc Phthalocyanine (ZnPc) comparing to pure ZnPc. Moreover, morphology has also been examined.

1.9 Thesis Layout

This thesis comprises of four chapters. Introduction of the research work, the problem statement as well as the proposed solution are given in chapter 1. In chapter 2,the experimental work done in fabrication and characterization of Antimony (Sb) doped zinc Phthalocyanine (ZnPc) thin film is explained. In chapter 3, results and discussions have been presented. In chapter 4, conclusion of the present work is described.

Chapter 2

Experimental Work

ZnPc:Sb/ITO devices were fabricated with varying concentration of antimony doped in ZnPc thin film in this experimental work. Different concentrations of Sb doped thin films of ZnPc were also sublimated on glasses. Optical and electrical characteristics, morphology and impedance spectroscopy were carried out after the evaporation of Al contacts.

Details are as follows.

2.1 Assembly of the hybrid thin films

Below are the schematic diagrams of thin films of ZnPc pasted on glasses and Al / ZnPc:Sb/ITO devices. For fabrication of the Al/ZnPC:Sb/ITO device, a piece of ITO is cut from the substrates by tungsten carbide cutter. Substrates of glass and ITO were prepared. Then these glass and ITO substrates were progressed to heat resistive high vacuum system for deposition of Znpc and Sb

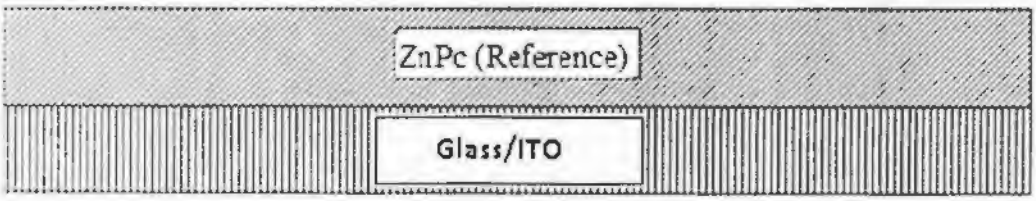

Figure 2.1: Assembly of thin film (a) ZnPc (Reference)

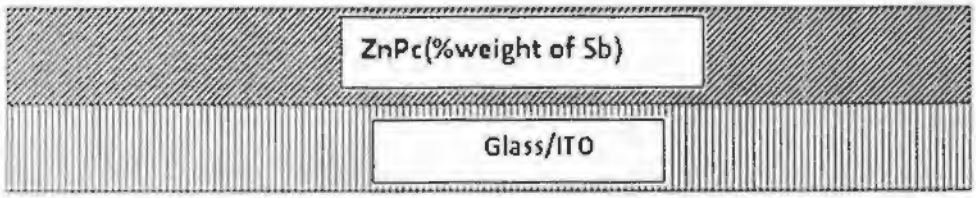

Figure 2.2: Assembly of thin film (b) ZnPc: Sb

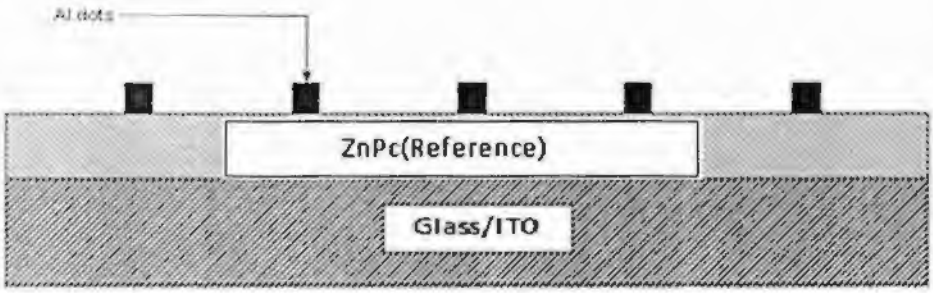

Figure 2.3: Assembly(a) Al/ZnPc/ITO (Reference)

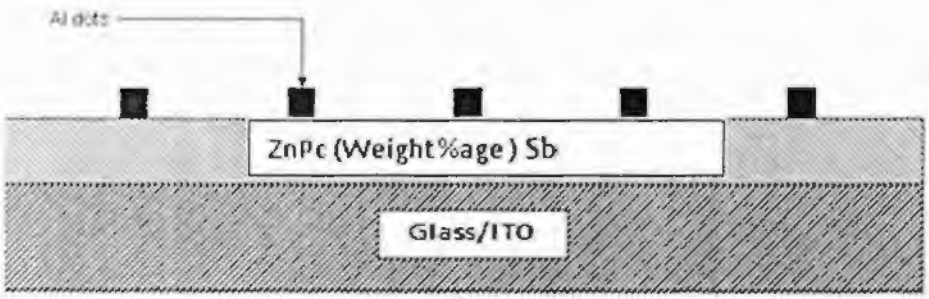

Figure 2.4: Assembly (b) Al/ZnPc:Sb/ITO

2.2 The Vacuum systems for deposition

Zinc Phthalocyanine (ZnPc) thin films doped with different weight percentage concentration of antimony (Sb) were pasted on ITO substrates and on glass substrates by using H.R high vacuum system(A 550V).Quartz micro balance (Gold crystal sensor) inside the chamber was used to observe thickness of deposited thin films. During deposition process, the base pressure was maintained at 4×10^{-6} mbar.

2.3 The substrate of ITO for Device Assembly

For the fabrication of hybrid devices, ITO substrates were provided by PCRET, Islamabad.

For fabrication of thin film devices,ITO coated glass is widely used as substrate due to its two main characteristics i.e. optical transparency and electrical conductivity.

ITO is tin oxide heavily doped with indium which makes it n-type with the band gap of about 4ev [16].It is transparent in the visible region of the spectrum.

ITO is broadly used in nanotechnology to fabricate solar cells. ITO based Solar cells are best because of their flexibility, cost effectiveness, light weight [17].

2.4 Antimony (Sb)

Antimony with symbol Sb is a chemical element with atomic number 51. A lustrous gray metalloid, found mainly in nature as the sulfide mineral stibnite. Its electron configuration is [Kr] 4d105s25p3 and was discovered in 3000 BC. Its atomic mass is 121.76 u ± 0.001 u and its melting point: 630.6 °C while the boiling point is 1,587 °C

2.4.1 Larger View of Antimony(Sb) Atom

The Sb atom consisting of 51 protons, 51 electrons and 71 neutrons has 5 energy levels. Electrons in the 1st orbit are 2 and in the remaining orbits are 8, 18, 18 and 5 respectively.

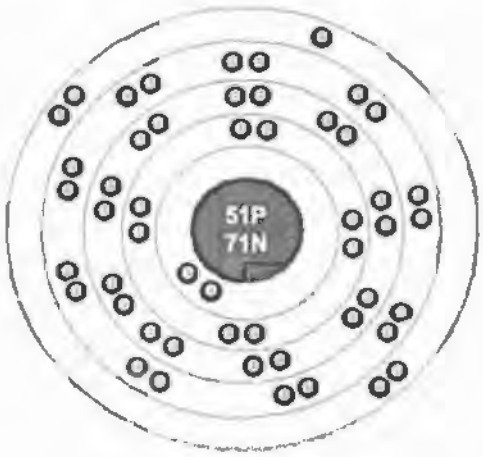

Figure 2.5: Position of Sb in Periodic Table of elements (b) Electronic Configuration

(a) (b)

2.4.2 Energy bands of metallic elements in Energy band theory.

Metallic elements are those in which valence and conduction bands largely overlap. There is no physical distinction between the two bands which indicates the availability of free electrons in abundance. Forbidden energy gap in good metallic conductor is negligible. Typical resistivities are given below [18].

Conductors	$10^{-8}\ \Omega.m$
Semiconductors	$10^{-3}\ \Omega.m$
Insulators	$10^{12}\ \Omega.m$

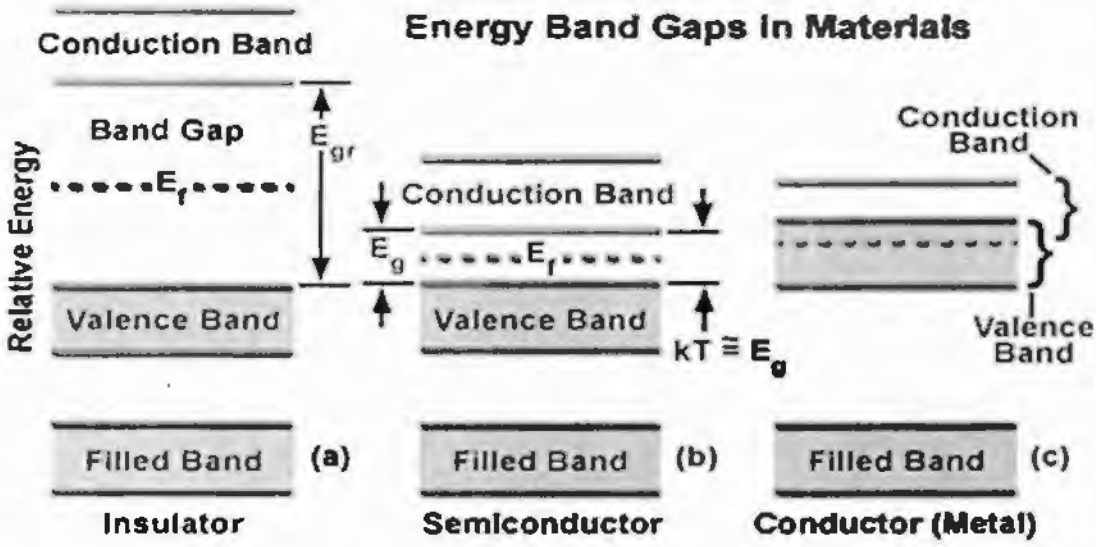

Figure 2.6: Comparison of insulators, conductors and semiconductor.

http://www.olympusmicro.com/primer/java/lasers/diodelasers/diodelasersfigure1.jpg

2.5 Phthalocyanine(Pc):

A macrocyclic compound in nature having bluish green color is widely used for dyeing. Most elements of the metals react with Phthalocyanines to form coordinate complexes. These complexes are also same in color as that of Pc's and broadly used in dyeing [19-21].

Due to excellent optical, electrical properties and thermal stability, Phthalocyanines have a wide range of application in material science [22-26].

Examples of Metal phthalocyanine:

Magnesium (II) phthalocyanine [Pc (Mg)]

Copper (II) phthalocyanine [Pc (Cu)]

Zinc (II) phthalocyanine [Pc (Zn)]

Cadmium (II) phthalocyanine [Pc (Cd)]

Titanium (III) phthalocyanine chloride [Pc(Ti)Cl]

2.6 Preparation of samples:

For the purpose of fabrication of Sb doped ZnPc thin films, ITO and glass Substrates were used.

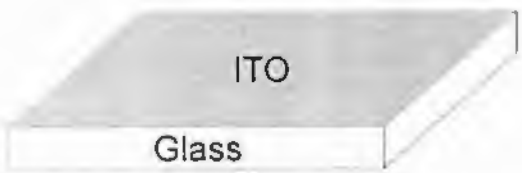

Figure 2.7: ITO Coated Substrate

The first step was etching of ITO partially from ITO substrate by placing it in HCL solution after covering the center part of ITO surface by a tape.

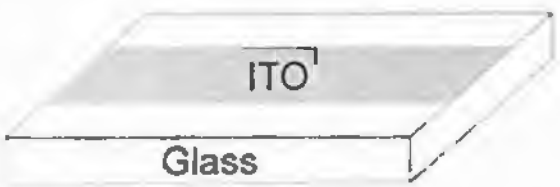

Figure 2.8: Partial ITO Removal

Substrates were then washed indetergent via sonication process, followed by sonication in Isopropyl Alcohol for 10min at 60℃. The same process was repeated for

ITO immersion ethanol for 10 min and then in acetone. Ultrasonic bath, Branson and Branson-E-Module was used for sonication process. The substrates were further rinsed with in de-ionized water.

After cleaning the substrates, ZnPc doped with different weight concentration of Sb was sublimated on one side of the ITO with thickness of about 200nm (ZnPc-Sb-ZnPc, Sandwich structure).

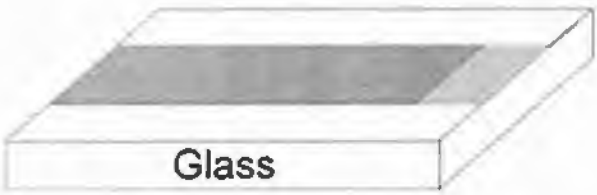

Figure 2.9: Deposition of Sb doped ZnPC on ITO

Aluminum (Al) metal was evaporated thermally on the whole one side surface of the ITO with thickness of 300 nm after masking it.

Figure 2.10: Deposition of Electrical contacts (Al)

Tungsten coil (Spiral) was used to evaporate Aluminum, where the ZnPc and Sb utilized a titanium boats in Heat Resistive high vacuum system. Base pressure was kept 4×10^{-6} mbar and deposition rate was (1 ~ 3) A°/s.

Five samples were prepared by varying the thickness of antimony. PCRET, Islamabad provided all the above mentioned fabrication facility along with material for the fabrication of Sb doped ZnPC thin films.

ZnPc with different concentration of antimony were deposited on glass substrates.

For reference unit of Zinc Phthalocyanine thin film, only pure ZnPc powder was deposited on ITO and glass substrates with a thickness of 200nm from titanium boat in vacuum chamber at base pressure 4×10^{-6}mbar. High vacuum (Heat Resistive) system, Leyhold-Heraeus (A 550V) was used in the whole physical vapor deposition technique.

Figure 2.11: High vacuum (Heat Resistive) system, Leybold-Heraeus (A 550V)

After the preparation, samples were characterized by using the following equipments

2.7 Test Equipments used

- Electrical properties determined by Electrometer, Keithley 2420.
- Optical properties determined by Spectrometer, Specord 200.

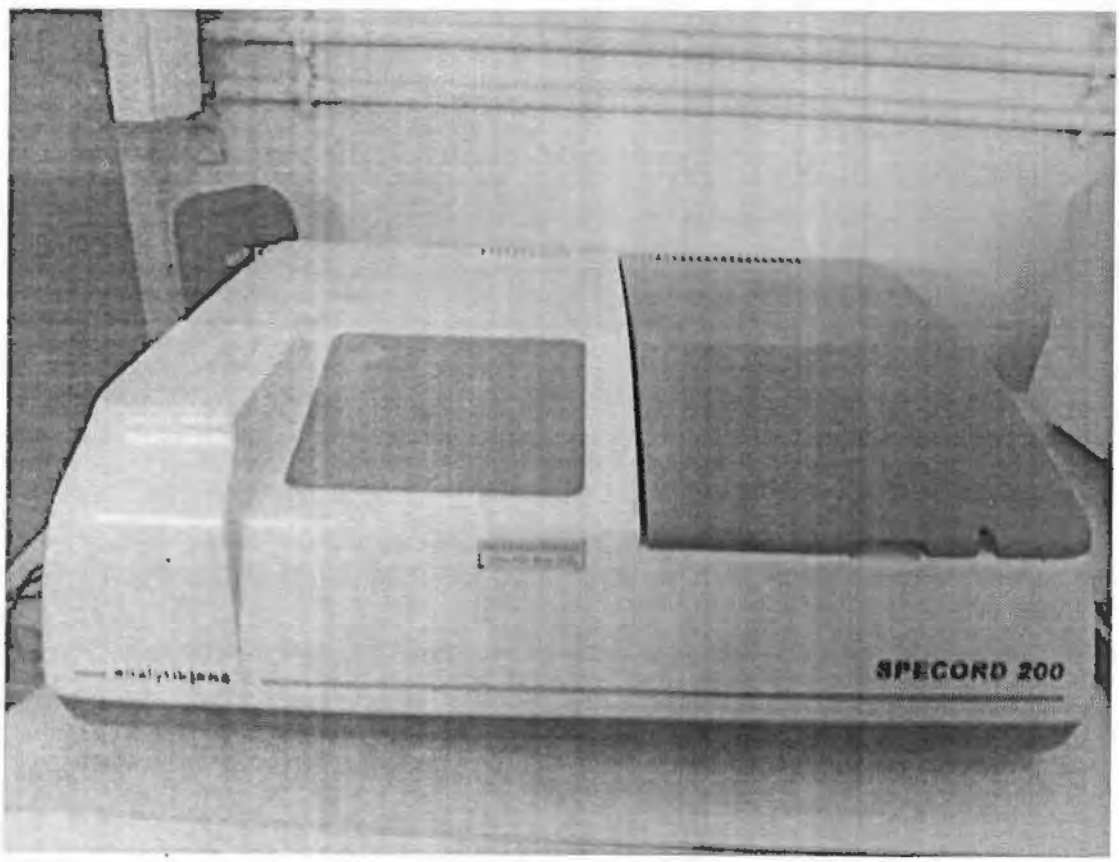

Figure 2.12: UV-Vis Apparatus SPECORD 200

Chapter 3

Results And Discussions

The complete aspect correlated to the characterization modes applied for the investigation of different parameters for depositing thin films e.g. morphological analysis with the help of EDX and SEM, electrical characterization i.e. I-V and J-V characteristics and optical characterization has been discussed in this chapter.

3.1 Energy Dispersive X-ray Spectroscopy (EDX)

For the morphological analysis of Zinc Phthalocyanine (Pure) and Zinc Phthalocyanine doped with varying mass percentage concentration of Antimony thin films SEM (field emission scanning electron microscope) was done using MIRA3 TESCAN model. It operates at accelerating voltage of 0.2 to 1kv and very high resolution images were produced.

We could see the change in weight percentage and atomic percentage of Sb in ZnPc thin film with the help of EDX. The images and tables below are showing all the elements including antimony (Sb) present in thin film with its weight percentage and atomic percentage in the five different samples of Zinc Phythalocyanine (ZnPc) which were prepared.

The EDX results are discussed including images and tables in forthcoming pages.

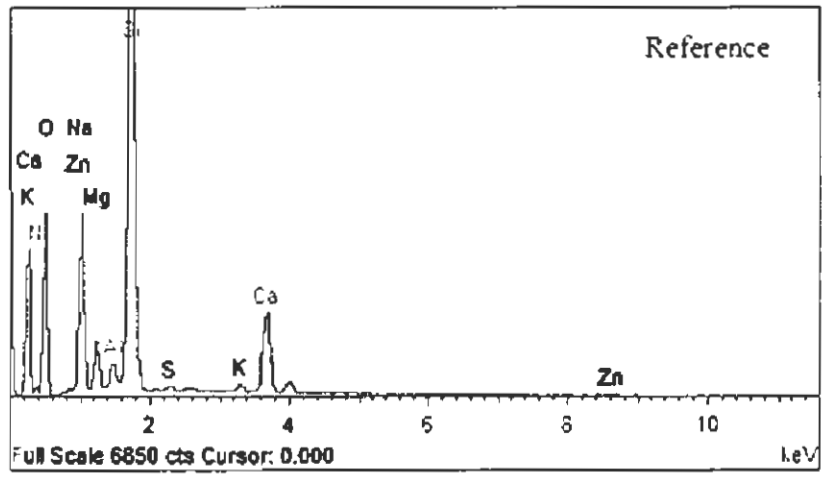

Figure 3.1: Reference Sample

The above figure 3.1 of the pure reference sample, was prepared with the help of EDX which shows the peaks of all the elements in the sample. It is evident from the result that no Antimony (Sb) is present. Below is the table 3-1 showing the weight percentage and atomic percentage of the elements in the reference sample.

Element	Weight%	Atomic%
N K	15.10	21.35
O K	34.82	43.11
Na K	8.32	7.17
Mg K	1.97	1.61
Al K	0.70	0.51
Si K	33.03	23.29
S K	0.22	0.14
K K	0.37	0.19
Ca K	5.08	2.51
Zn K	0.38	0.12
Totals	100.00	

Table 3-1: Weight and Atomic percentages of the elements in reference sample

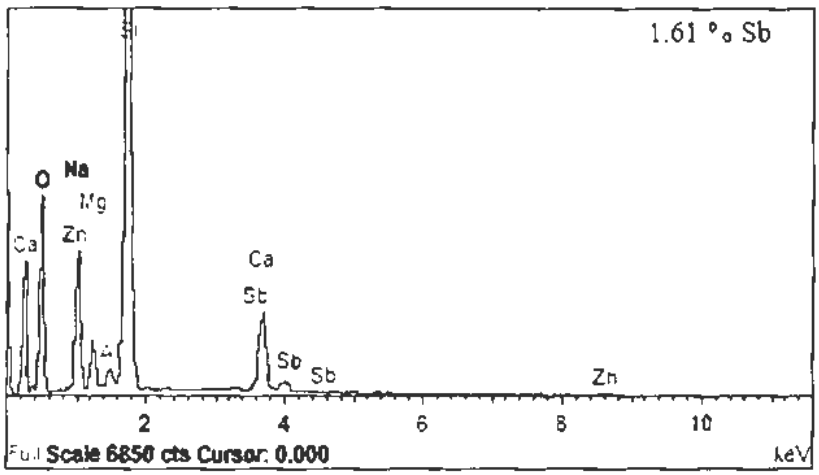

Figure 3.2: Peaks of Sb (1.61%)

The above figure 3.2 is of the doped ZnPc sample with antimony showing peaks of the elements. From the details listed in the table 3-2, it is evident that the weight percentage of Antimony (Sb) is 1.61% and the atomic percentage is 0.29%.

Element	Weight%	Atomic%
O K	40.92	55.35
Na K	8.54	8.04
Mg K	2.44	2.17
Al K	0.59	0.48
Si K	39.10	30.13
Ca K	6.20	3.35
Zn K	0.60	0.20
Sb L	1.61	0.29
Totals	100.00	

Table 3-2 Weight and Atomic percentages of all elements in 1.61% Sb sample

After adding 1.61% weight percentage of Sb, the bandgap was decreased to 1.73 from 1.86 ev.

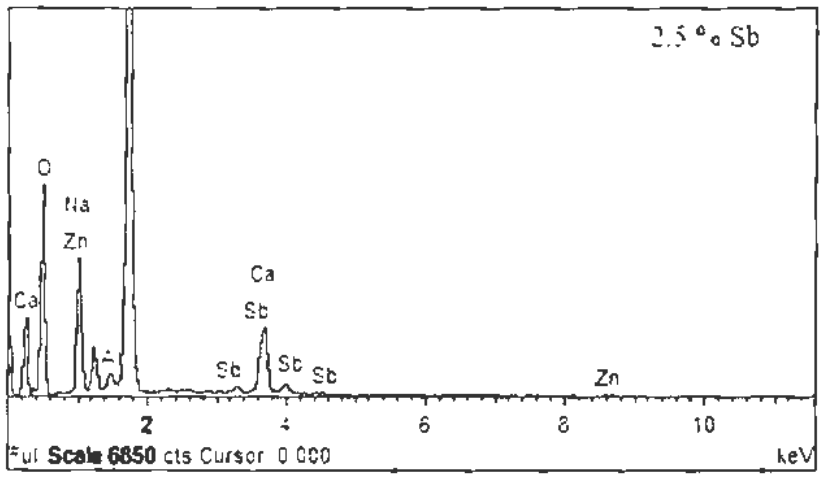

Figure 3.3: Peaks of Sb (2.5%)

The above figure 3.3 from the EDX shows the peaks of elements in Sb 2.5% sample. From the details mentioned below in table 3-3, it is evident that the weight and atomic percentage of antimony has increased to 2.5% and 0.40% in the ZnPc thin film. The energy bandgap was also decreased to 1.651 ev.

Element	Weight%	Atomic%
O K	61.82	74.27
Na K	21.88	18.29
Al K	2.56	1.82
Ca K	10.33	4.95
Zn K	0.92	0.27
Sb L	2.50	0.40
Totals	100.00	

Table 3-3: Weight and Atomic percentages of the elements in 2.5% Sb sample

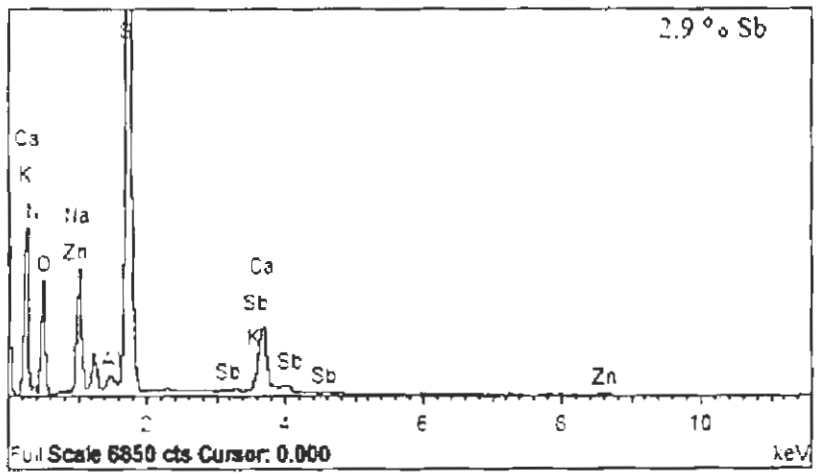

Figure 3.4: Peaks of Sb (2.9%)

The above figure 3.4 from the EDX showing the peaks and the table mentioned below is showing the quantity of elements where we can see that the weight percentage and atomic percentage of antimony has increased to 2.9% and 0.47%.The energy bandgap was 1.620 for this sample.

Element	Weight%	Atomic%
N K	21.54	30.18
O K	31.72	38.92
Na K	7.31	6.24
Al K	0.41	0.30
Si K	30.40	21.25
K K	0.18	0.09
Ca K	4.76	2.33
Zn K	0.78	0.24
Sb L	2.90	0.47
Totals	100.00	

Table 3-4: Weight and Atomic percentages of the elements in 2.90% Sb sample

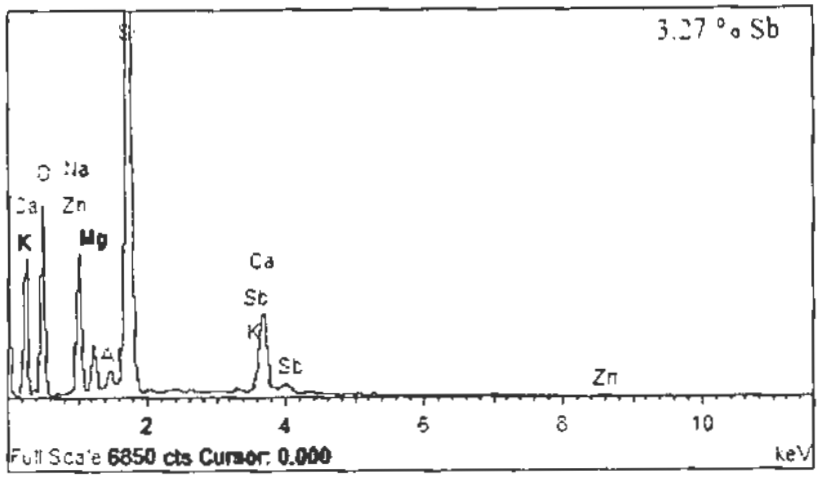

Figure 3.5: Peaks of Sb (3.27%)

The above figure 3.5 and the below table 3-5 from the EDX, shows that the weight percentage and atomic percentage of antimony has increased to 3.27% and 0.59 in the ZnP:Sb thin film.

Element	Weight%	Atomic%
O K	39.37	54.35
Na K	8.56	8.23
Mg K	2.34	2.12
Al K	0.57	0.47
Si K	38.60	30.36
K K	0.30	0.17
Ca K	6.34	3.49
Zn K	0.65	0.22
Sb L	3.27	0.59
Totals	100.00	

Table 3-5: Weight and Atomic percentages of the elements in 3.27% Sb sample

3.2 Electrical characterization of Zinc Phthalocyanine thin films doped with (Sb)

For analyzing the current density-voltage (J-V) characterization, we used Electrometer Keithley 2420 and essentials of I-V measurements were recorded to PC computer. The current density and voltage characterization is given in Figure 3.6

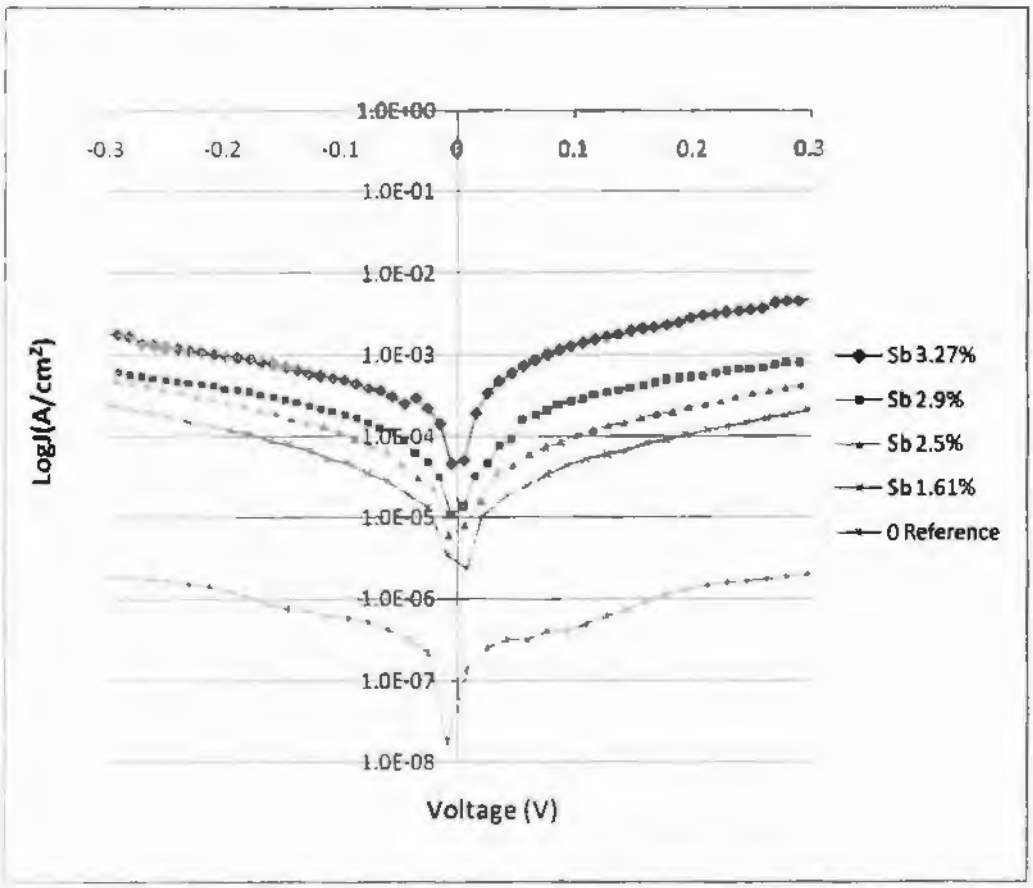

Figure 3.6: J-V data obtained for Al/ZnPc:Sb/ITO device

For the electrical characterization the potential difference was varied from -0.3v to 0.3v across the device. The results of all the thin films are shown in Figure-3.6. It is observed that the conductivity has increased with the increase of Sb

contents in ZnPc. This increase in the conductivity is attributed to the Sb content which is good conductor while ZnPc is a semiconductor material.

To check the conduction mechanism for this biasing region, graph between Log J versus Log V were plotted for all the thin films and the slop was calculated. The slops of the entire plot are less than 2 whicb confirm that the schottky type conduction mechanism [21]. The contribution of higher voltages on J-V characteristics of the device was analyzed by plotting the graph between the logs of "J" and "V" as shown below in figure 3.7

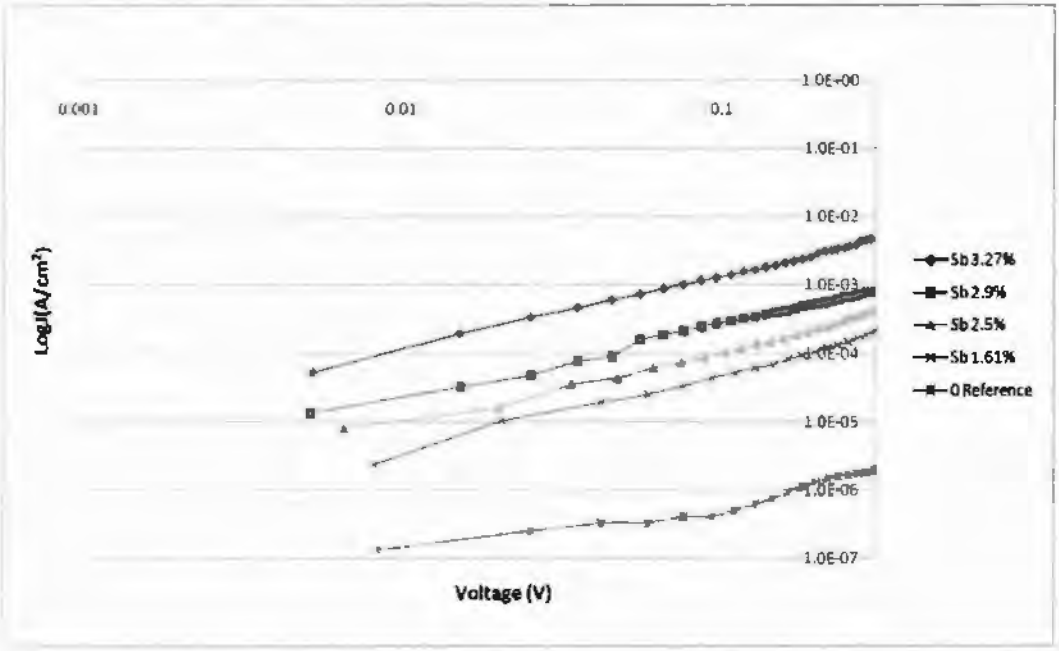

Figure 3.7: Log (J)-log (V) data obtained for Al/ZnPc:Sb/ITO device

3.3 Optical characterization of thin films of Zinc Phthalocyanine doped with a variety of weight concentration of Antimony

The optical band gaps were deliberated in figures 3.8 to 3.12 and given in the table3-6. From the outcomes of the graphs it is evident that the optical band gap was

decreased with mounting the doping of antimony in Zinc Phthalocyanine. The value of band gap for pure ZnPc (Reference) was 1.86 while after adding the 3.27 weight %age of Sb in ZnPc it reached at 1.58. Furthermore, it can also be evidently seen in the graph that the width of the absorbance window was increased with increasing the doping level of Sb in ZnPc.

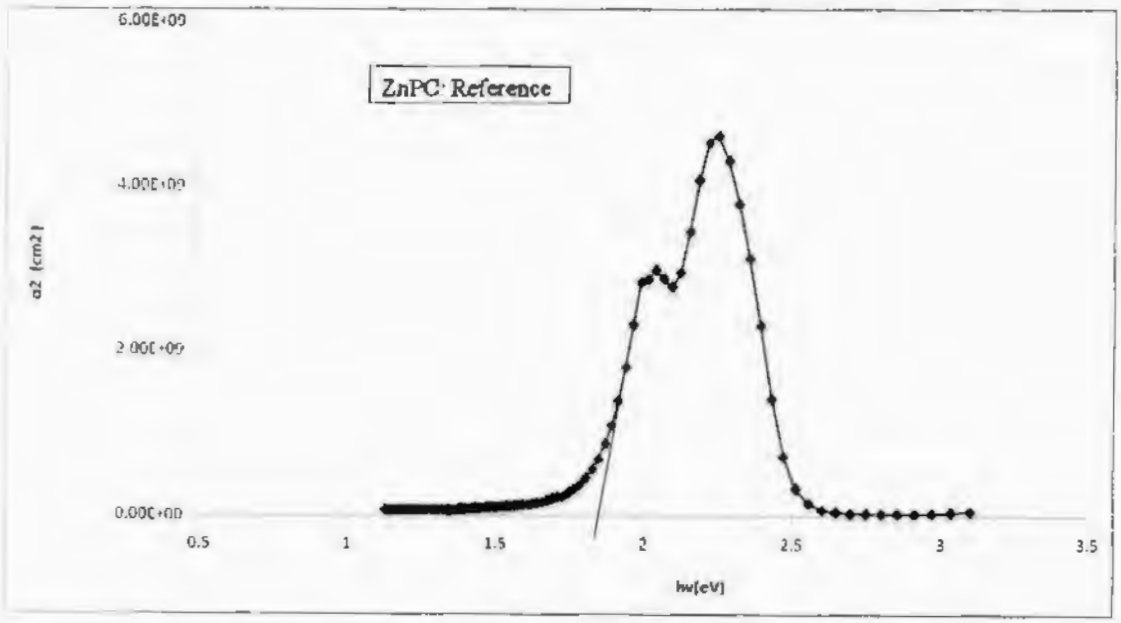

Figure 3.8: Graph for band gap of ZnPc (Reference)

From the above graph it is evident that the bandgap of ZnPc of 200 nm thickness is 1.86ev. To reduce this bandgap, is the main target. This target will be achieved by doping different levels of antimony (Sb) in ZnPc thin film.

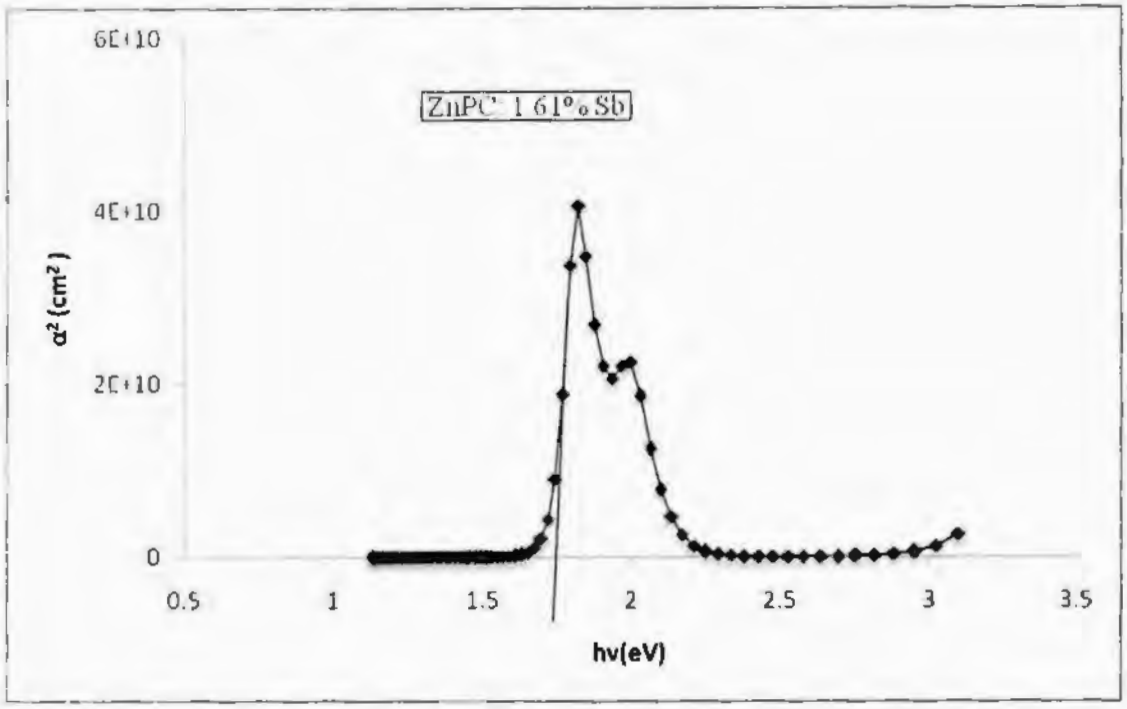

Figure 3.9: Graph for band gap of ZnPc: 1.61 weight %age of Sb

The above graph shows the bandgap of ZnPc thin film after doping it with antimony (Sb). The value of the bandgap is 1.73ev. It shows that the bandgap was decreased from 1.86 to 1.73 after adding 1.61% of Sb weight percentage. This value of bandgap decreases more by adding more amount of antimony in it.

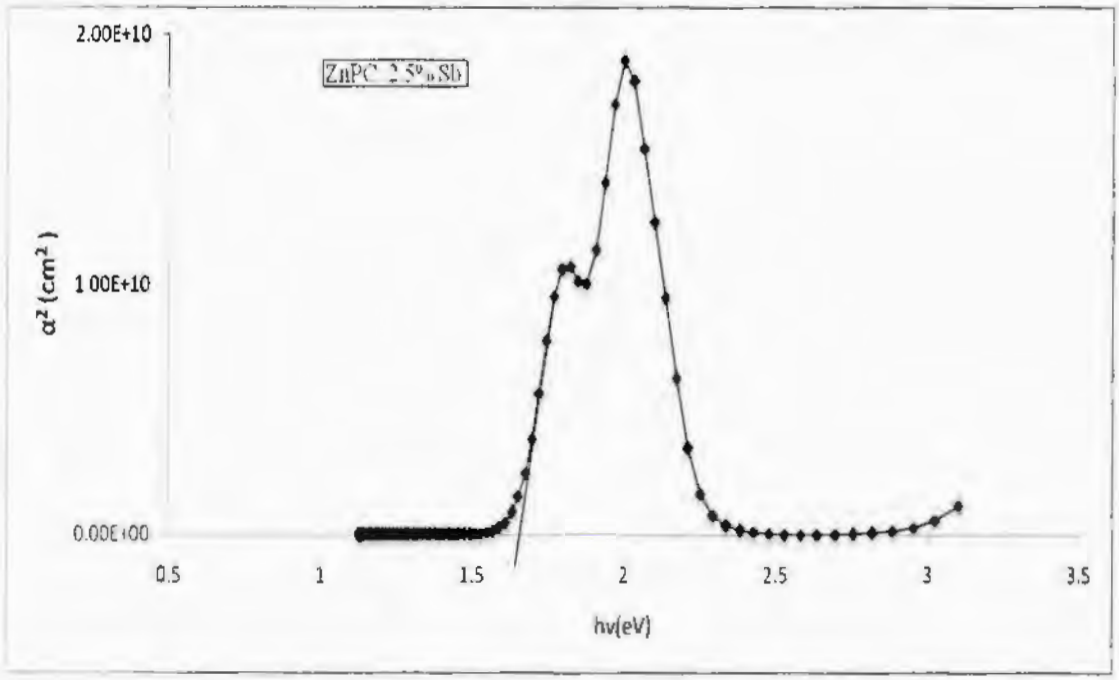

Figure 3.10: Graph for band gap of ZnPc: 2.5 weight %age of Sb

The above graph shows the bandgap of ZnPc thin film after doping it with antimony (Sb). The value of the bandgap in above graph is 1.651ev. It shows that the bandgap was decreased from 1.86 to 1.651 after adding 2.5% of Sb weight percentage in Zinc Phthalocyanine (ZnPc) thin film.

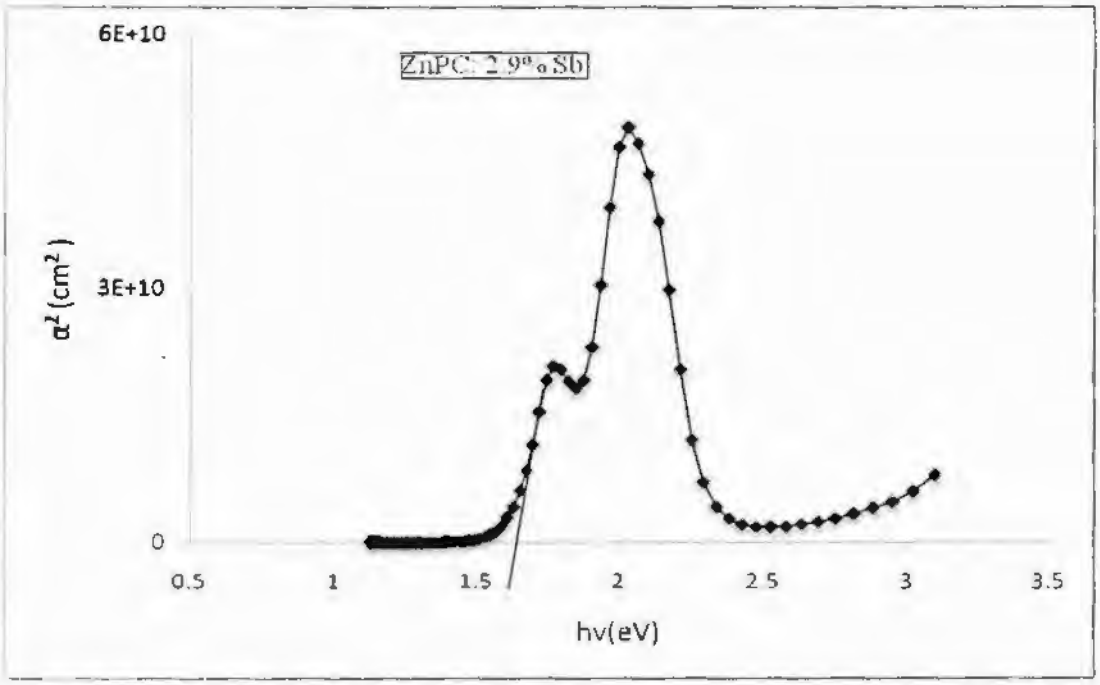

Figure 3.11: Graph for band gap of ZnPc: 2.9 weight %age of Sb

The above graph shows the bandgap of ZnPc thin film after doping it with antimony (Sb). The value of the bandgap in above graph is 1.620ev. It shows that the bandgap was decreased from 1.86 to 1.620 after adding 2.9% of Sb weight percentage in Zinc Phthalocyanine (ZnPc) thin film.

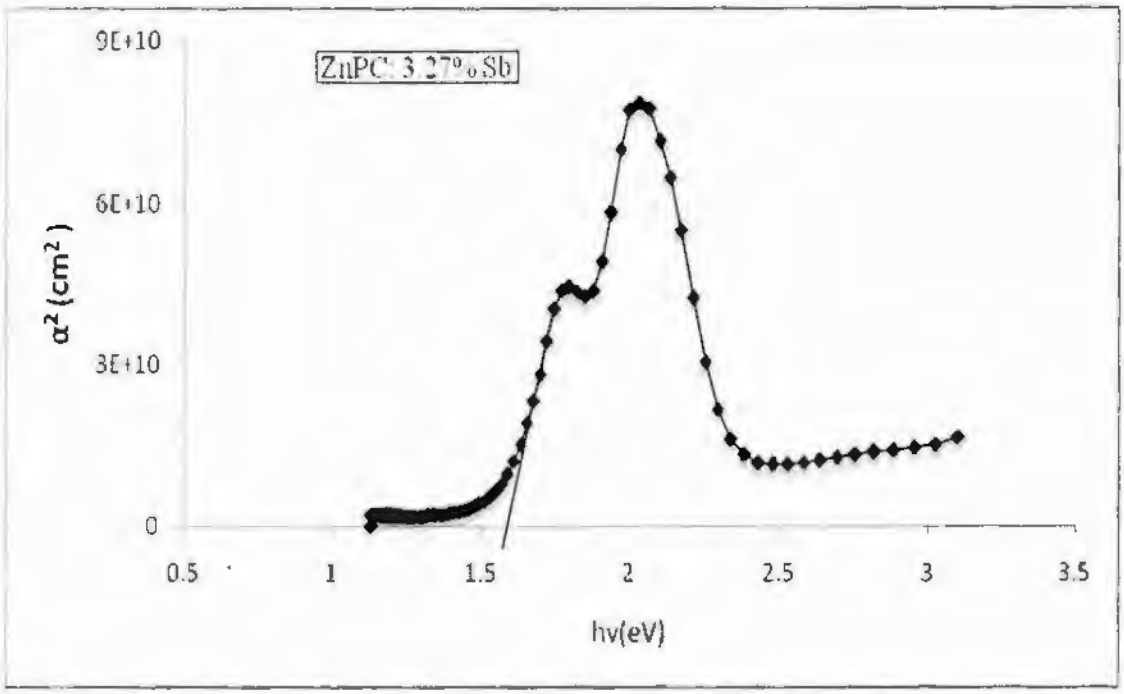

Figure 3.12: Graph for band gap of ZnPc: 3.27 weight %age of Sb

The above graph shows the bandgap of ZnPc thin film after doping it with antimony (Sb). The value of the bandgap in above graph is 1.58ev. It shows that the bandgap was decreased from 1.86 to 1.58 after adding 3.27% of Sb weight percentage in Zinc Phthalocyanine (ZnPc) thin film.

Badge No	Sample	Weight %age of Sb	Thickness of ZnPc (nm)	Bandgap
1	ZnPc (Reference)	0	200	1.86
2	ZnPc: (1.61)%Sb	1.61	200	1.73
3	ZnPc: (2.5)%Sb	2.5	200	1.651
4	ZnPc: (2.9)%Sb	2.9	200	1.620
5	ZnPc: (3.27)%Sb	3.27	200	1.58

Table 3-6: Optical Band gapes

This band gap decrease can be attributed to the fact that after adding the Sb in ZnPc the interstitial states were introduced and hence increased the absorption of more and more photons, which results the widening of absorption window, which has been observed in the results as shown in figure 3.13

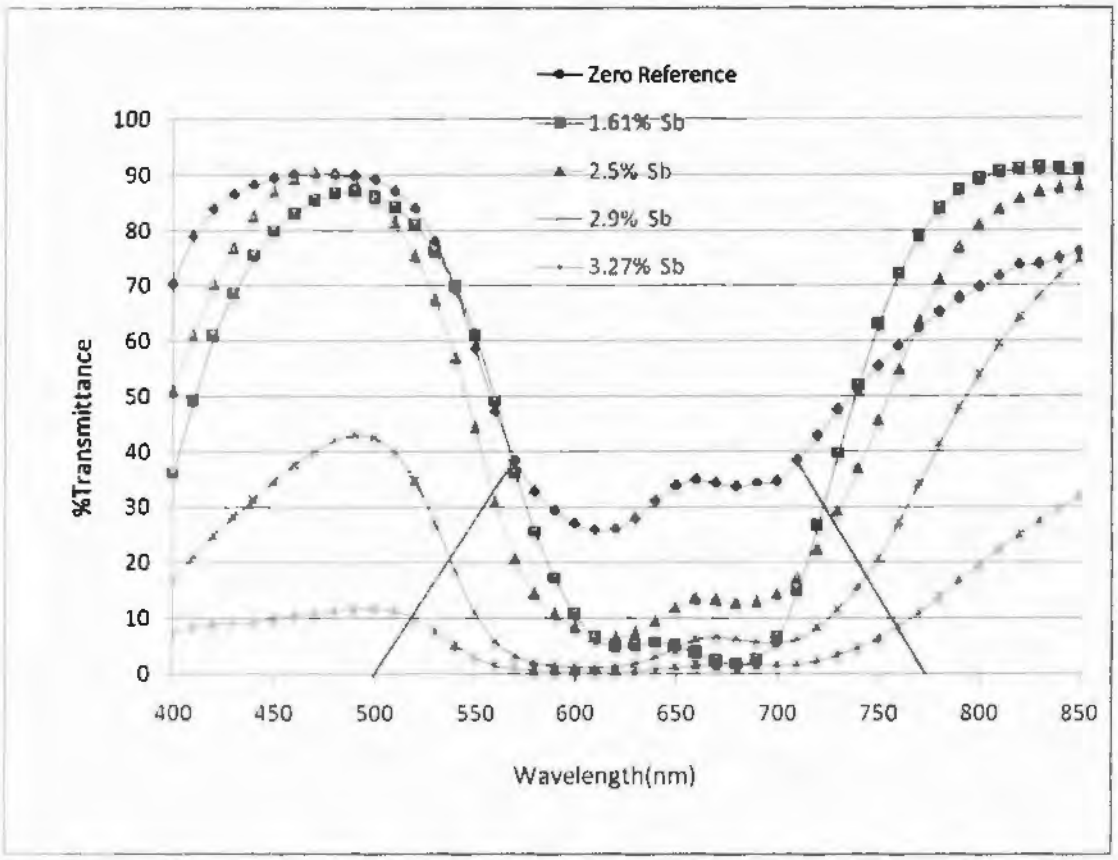

Figure 3.13: Comparison graph for widening of absorbance window

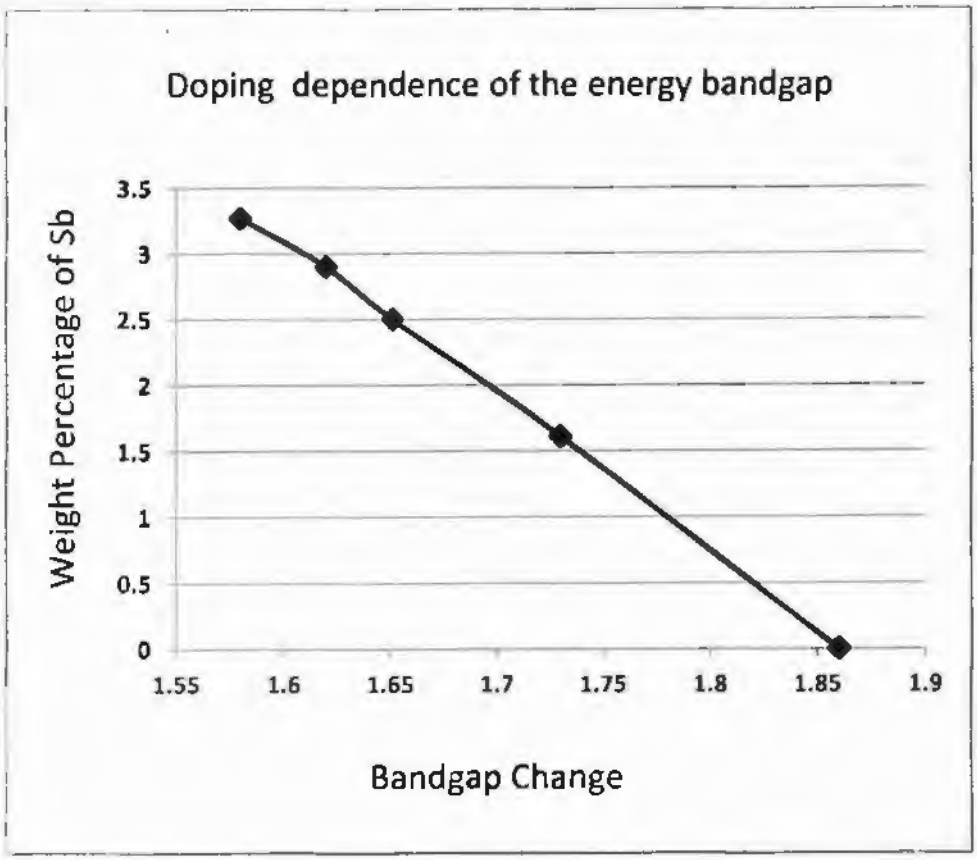

Figure 3.14: change in band gap energy with doping concentration of Sb

It is evident from the result in above figure 3.14 that the increasing percentage doping of Sb causes to shrink the band gap of thin films. We may explain this effect by the fact that the impurity atoms begin to overlap as the percentage of the impurities increase.

3.4 Morphological Analysis of ZnPc thin films by SEM

The surface morphology images through SEM show that the surface morphology is same throughout the performance. A slight change has occurred between the morphology of ZnPc(pure) and ZnPc with varying mass percentage concentration of Sb. These images show that the particle size has decreased by increasing the weight percentage of Sb from 0% to 3.27%. These images can be seen below.

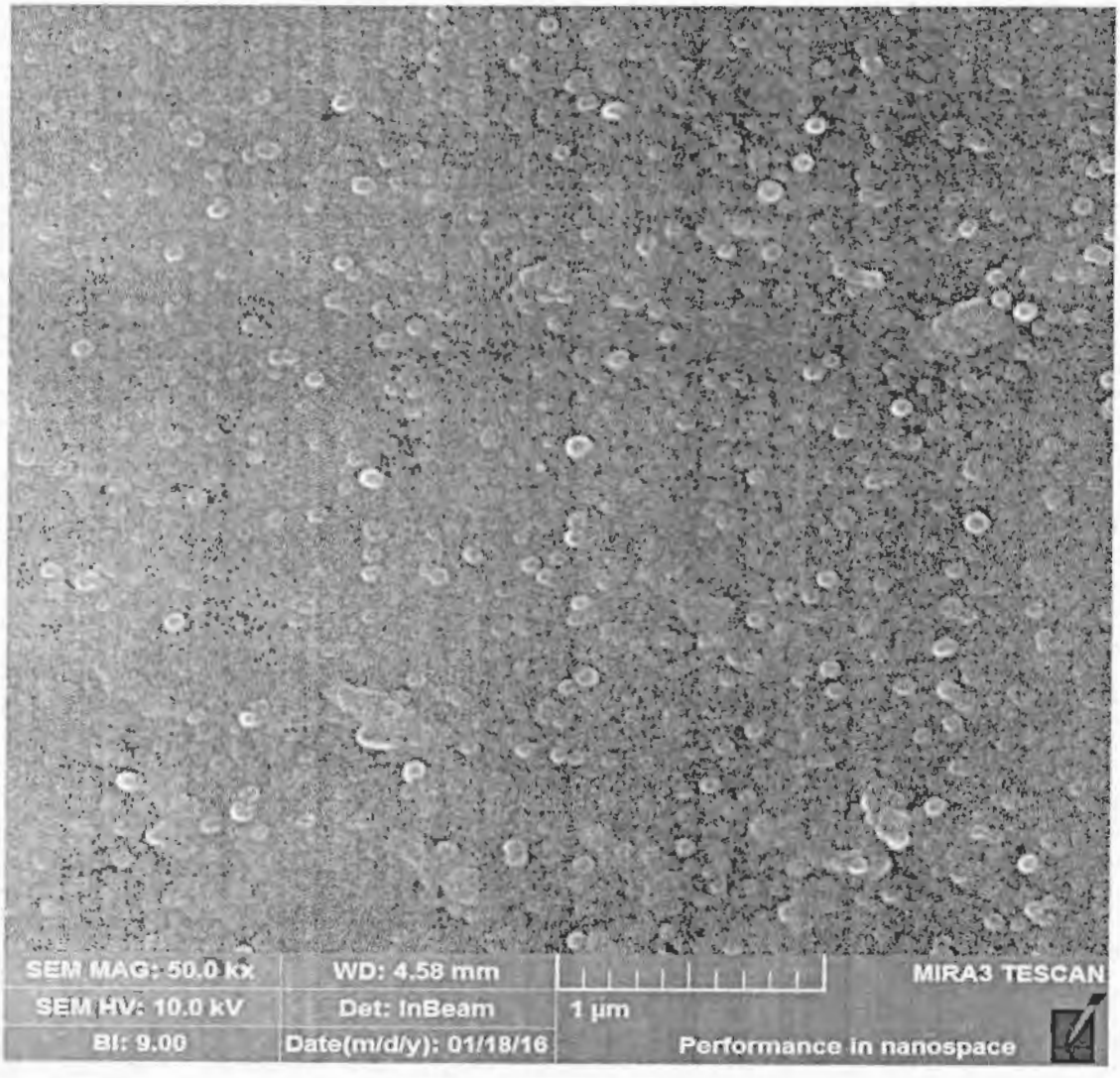

Figure 3.15: SEM of ZnPc (Reference)

The above figure 3.15 from the SEM shows the surface morphology of the reference sample having 200 nm of ZnPc.

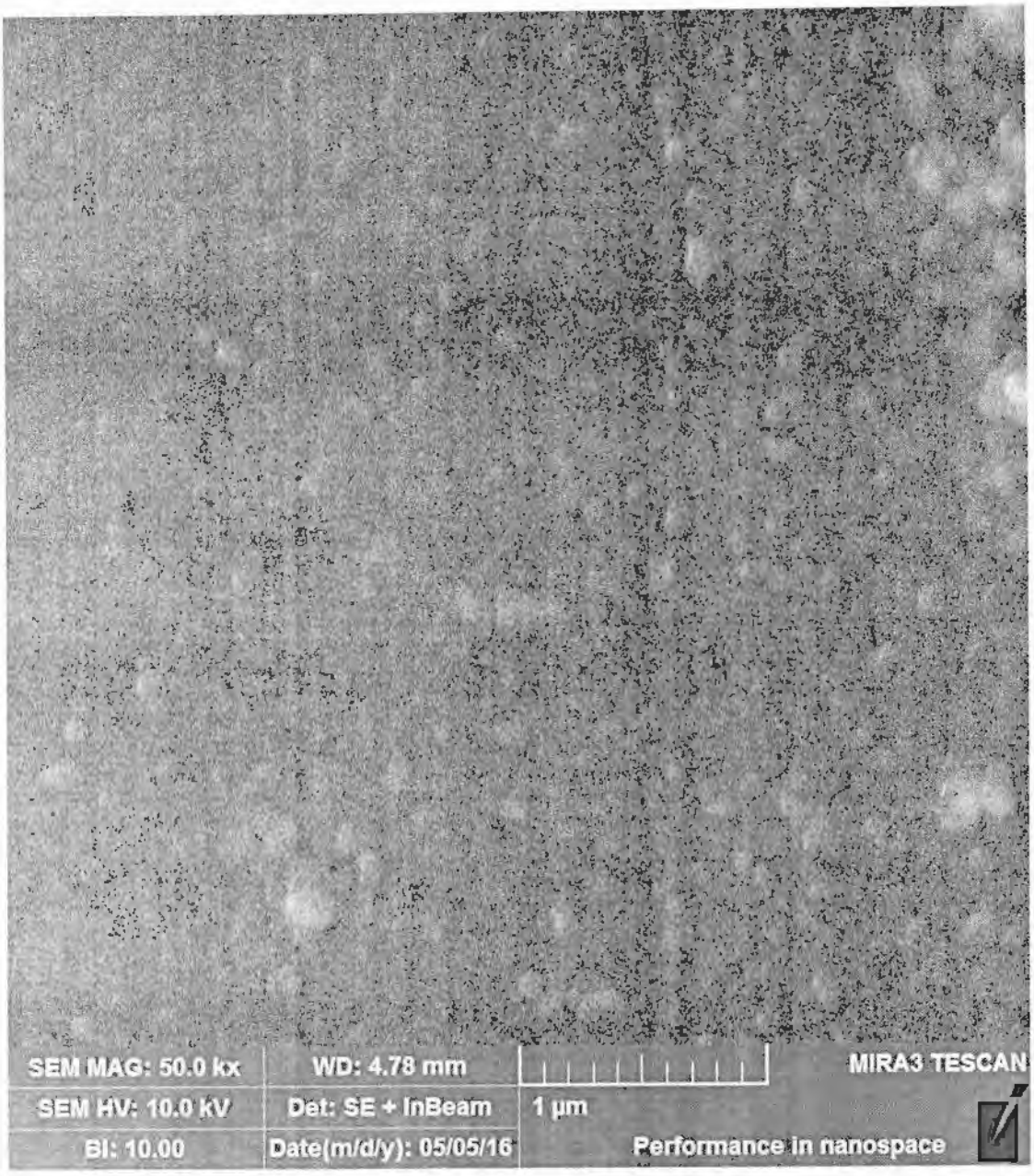

Figure 3.16: SEM of ZnPc: 3.27 weight % of Sb

The above figure 3.16 from the SEM shows the surface morphology of the sample having 3.27% weight percentage of antimony. It was observed that with the increase in weight percentage of Sb the morphology of the surface was same but the particle size decreased.

Chapter 4

Summary And Conclusion

Zinc phthalocyanine (ZnPc) is a promising candidate for solar-cell applications, because it is easily synthesized and is non-toxic to the environment. In the visible region of the electromagnetic spectrum, antimony(Sb) doped zinc phthalocyanine(ZnPc) thin films exhibits a good absorption.

In this study, antimony (Sb) with different weight concentration doped with Zinc Phythalocyanine (ZnPc) thin films was sublimated on ITO coated glass substrates by heat resistive high vacuum evaporation system. Five samples were prepared by varying the thickness of antimony.

Different characterizations of fabricated ZnPc:Sb thin films were then performed. The doping percentage was confirmed by Energy Dispersive X-ray spectroscopy (EDX). Through electrical characterization the current density and voltage characterization were calculated. By optical characterization, transmittance percentage and wavelength were recorded for the calculation of absorbance window and optical band gaps. For morphological analysis, SEM (field emission scanning electron microscope) was done.

From all the above characterizations, the results of ZnPc thin films doped with varying weight concentration of Sb are mentioned below:

- Energy Dispersive X-ray spectroscopy (EDX) results have shown that the weight percentage of antimony (Sb) contents in the samples are 0%, 1.61%, 2.5%, 2.9% and 3.27% and the atomic percentages in the samples are 0%, 0.29%, 0.40%, 0.47% and 0.59% which confirms the doping of antimony (Sb) contents in ZnPc.
- Current Voltage (IV) results, recorded by varying the voltage from -0.3v to 0.3v, shown that the conductivity increases with the increase antimony (Sb) contents in Zinc Phthalocyanine (ZnPc) thin film.
- The conduction mechanism was confirmed by plotting the graph of Log(J) against Log(V). Slope of the graph was calculated as less than 2 which shows that the conduction mechanism is Schottky type.
- The graph between transmittance and wavelength (nm) shows that the absorbance window is increased from 140nm to 240nm with increasing amount of Sb contents in ZnPc thin film. This increase in absorbance window was calculated by plotting the graph and then by drawing intercepts on wavelength axis.
- Energy bandgap calculated by plotting the graph between E_g and α^2 shows that optical band gap is 1.86ev, 1.73ev, 1.651ev, 1.62ev and 1.58ev in the samples as the antimony (Sb) contents increased from 0 to 3.27%, showing the intermediate states development in the sample. This band gap was measured on each sample values by first plotting the graph of E_g and $\alpha^2$and then taking the intercepts on energy axis.

- The morphological analysis of the SEM micrographs shows the shapes of the particles were spherical and the average size was decreased as Sb weight percentage increased from 0% to 3.27% in ZnPc thin film.
- From the above stated results it can be concluded that antimony (Sb) doping in Zinc Phthalocyanine (ZnPc) thin films increases the absorption and conductivity and decreases the bandgap which made it a good candidate for solar cell applications.

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