# MULTIFUNCTIONAL APPLICATIONS OF SINGLE CRYSTAL AND NANOMATERIALS OF TOPOLOGICAL INSULATOR Bi<sub>2</sub>Se<sub>3</sub>

**Ph.D.** Thesis

By KUSHAL MAZUMDER



## DISCIPLINE OF PHYSICS INDIAN INSTITUTE OF TECHNOLOGY INDORE FEBRUARY 2020

# MULTIFUNCTIONAL APPLICATIONS OF SINGLE CRYSTAL AND NANOMATERIALS OF TOPOLOGICAL INSULATOR Bi<sub>2</sub>Se<sub>3</sub>

## A THESIS

Submitted in partial fulfillment of the requirements for the Award of the degree Of DOCTOR OF PHILOSOPHY

> By KUSHAL MAZUMDER ROLL NO: PHD1401251003



# DISCIPLINE OF PHYSICS INDIAN INSTITUTE OF TECHNOLOGY INDORE FEBRUARY 2020



## INDIAN INSTITUTE OF TECHNOLOGY INDORE

### **CANDIDATE'S DECLARATION**

I hereby certify that the work which is being presented in the thesis entitled MULTIFUNCTIONAL APPLICATIONS OF SINGLE CRYSTAL AND NANOMATERIALS OF TOPOLOGICAL INSULATOR Bi<sub>2</sub>Se<sub>3</sub> in the partial fulfillment of the requirements for the award of the degree of DOCTOR OF PHILOSOPHY and submitted in the DISCIPLINE OF PHYSICS, Indian Institute of Technology Indore, is an authentic record of my own work carried out during the time period from December, 2014 to February, 2020 under the supervision of Dr. Parasharam M. Shirage, Associate Professor, Discipline of Metallurgy Engineering and Materials Science.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

Signature of the student with date (KUSHAL MAZUMDER)

This is to certify that the above statement made by the candidate is correct to the best of my/our knowledge.

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Signature of Convener, DPGC Date: 29-05-2020

## ACKNOWLEDGEMENTS

First and foremost, I would like to express my deep and sincere gratitude to my supervisor Dr. Parasharam M. Shirage, Associate Professor, IIT Indore, for giving me the opportunity to do research and providing me with profound comments, guidance and constant encouragement, and support throughout my Ph.D. study. His dynamism and enthusiasm towards work have deeply encouraged me to work more energetically and passionately. He is not only an advisor of my research but also a friend and mentor of my whole life and future endeavour career.

I would like to extend my sincere gratitude to my PSPC members Dr. Somaditya Sen, Discipline of Physics and Dr. Rupesh S. Devan, Discipline of Metallurgy Engineering and Materials Science, IITI, for their encouragement and invaluable suggestions. I also thank Dr. Sunil Kumar and Dr. S. Sen's group for providing suggestions and help during the experimental work.

During my Ph.D. years, I was fortunate enough to get financial support from IIT Indore and DST, Govt. of India for providing me the INSPIRE fellowship. I owe my sincere thanks to Discipline of Physics, IITI for providing the generous funding, laboratory facilities and rich environment to explore new ideas. I am also grateful to all the academic and administrative staff of IITI for providing practical support with friendly enthusiasm and grace. I thank Mr. Kinney Pandey and Nitin Upadhyay for helping me in the technical works at SIC Indore.

I am incredibly grateful to my colleague Alfa Sharma with whom I learnt the experimental works. I thank him for his constant encouragement and contribution in accomplishing my research. It has always been a great pleasure for me to work with him. I am also thankful to my friends and lab mates Yogendra, Manojit, Lichchhavi, Alfa, Prateek, Rukshana, Akshay, Amit and Subhash for their co-operation and support during my Ph.D. work.

I gratefully acknowledge Dr. Maulindu Kumar Chattopadhyay, Dr. S B Roy, RRCAT Indore and BARC Mumbai for permitting me to use their facilities at their institute. I would like to acknowledge Pune University, IUC Indore for the various kinds of characterizations facilities. I am also grateful to Dr. Rajeev Rawat, UGC DAE CSR Indore for providing the characterization facilities.

I am always thankful to my best buddies Dipayan, Mithun and Rinki for their moral support during my good as well as awful times and being my constant source of encouragement and confidence. Now a days, in this competitive world it's very hard to find friends with whom you share the lab space, on that note I am indebted to Manojit, Lichchhavi, Prateek and Alfa for their time and energy (not to mention many treats) they spent on me for my upbringing in our AFMRG lab.

Most importantly, I owe my heartfelt gratitude to my immediate family; Mother, Father, siblings and extended family, without whom none of this was possible. My family was a continuous source of love, concern, care and strength during these years.

On a very special note I extend regards from the core of my heart to my Mother (Maa) and Father (Baba) for their encouragement and inspiration.

Date: 19-02-2020

Kushal Mazumder

Dedicated

To my parents

Benu Mazumder Hnd

Basudev Mazumder

## LIST OF PUBLICATIONS

#### PAPER - 1

**Kushal Mazumder**, Alfa Sharma, Yogendra Kumar, Prashant Bankar, Mahendra A More, Rupesh Devan and Parasharam M. Shirage, Enhancement of field electron emission in topological insulator Bi<sub>2</sub>Se<sub>3</sub> by Ni doping, *Phys. Chem. Chem. Phys.* **20**, 18429-18435, 2018.

### PAPER - 2

**Kushal Mazumder**, Alfa Sharma, Yogendra Kumar and Parasharam M. Shirage, Effect of Cu intercalation on humidity sensing properties of Bi<sub>2</sub>Se<sub>3</sub> topological insulator single crystals, *Phys. Chem. Chem. Phys.*, **20**, 28257-28266, 2018.

### PAPER - 3

**Kushal Mazumder**, Maulindu K. Chattopadhyay and Parasharam M. Shirage, Electrical and magnetic properties of copper intercalated topological insulator Bi<sub>2</sub>Se<sub>3</sub> single crystal, *J. Supercond. Nov. Magn.*, **33**, 847-857, 2020.

#### PAPER - 4

**Kushal Mazumder**, Alfa Sharma, Yogendra Kumar and Parasharam M. Shirage, Temperature dependent I-V characteristics of Ni doped topological insulator Bi<sub>2</sub>Se<sub>3</sub> nanoparticles, *AIP Conference Proceedings*, **2115**, 030147 1-4, 2019.

#### PAPER - 5

Alfa Sharma, **Kushal Mazumder**, Yogendra Kumar and Parasharam M. Shirage, Synthesis and humidity sensing behaviour of Cu-intercalated Bi<sub>2</sub>Se<sub>3</sub> topological insulator single crystals, *AIP Conference Proceedings*, **2115**, 030407 1-4, 2019.

### LIST OF PUBLICATIONS (Other than the thesis)

### PAPER - 1

Alfa Sharma, Yogendra Kumar, **Kushal Mazumder**, Amit Kumar Rana and Parasharam M Shirage, Controlled  $Zn_{1-x}Ni_xO$  nanostructures for an excellent humidity sensor and a plausible sensing mechanism, *New J. Chem.*, **42**, 8445–8457, 2018.

# LIST OF CONFERENCE/WORKSHOP ATTENDED

**1.** Participated in RSc Symposium on "*Advances in Chemical Sciences*", at Indian Institute of Technology Indore, Indore, India 30<sup>th</sup> January, 2018.

**2.** Poster presentation at "*International Conference on Magnetic Materials and Applications (ICMAGMA)*", National Institute of Science Education and Research, Bhubaneshwar, India 9<sup>th</sup> – 13<sup>th</sup> December 2018.

**3.** Poster presentation at "*International Conference on Complex and Functional Materials (ICCFM)*", S. N. Bose National Centre for Basic Sciences, Kolkata, India 13<sup>th</sup> – 16<sup>th</sup> December 2018.

**4.** Poster presentation at "*Department of Atomic Energy, Solid State Physics Symposium (DAESSPS)*", Guru Jambeshwar University, Hisar, India 18<sup>th</sup> – 23<sup>rd</sup> December 2018.

 Poster presentation at "First Indian Materials Conclave, Material Research Society of India (MRSIAGM)", Indian Institute of Science, Bangalore, India 12<sup>th</sup> – 15<sup>th</sup> February 2019.

**6.** Global Initiative of Academic Networks (GIAN) workshop on "*Physics of Strongly Correlated Electron Systems*", at Bharathidasan University, Tiruchirappalli, India 19<sup>th</sup> – 23<sup>rd</sup> December 2016.

**7.** GIAN workshop on "*High-Pressure Synthesized Materials: A Chest of Treasure and Hints*", at Indian Institute of Technology Indore, India 11<sup>th</sup> – 19<sup>th</sup> July 2016.

**8.** GIAN workshop on "*Chemical Sensors: Principles, Technologies and Applications*", at Indian Institute of Technology Indore, India 1<sup>st</sup> – 9<sup>th</sup> July 2016.

**9.** Poster presentation at *"Ramanujan Conclave"*, at Indian Institute of Technology Indore, India  $22^{nd} - 23^{rd}$  December, 2015.

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## NOMENCLATURE

## Α

A Ampere Ag Silver Al Aluminium Au Gold В Bi<sub>2</sub>Se<sub>3</sub> Bismuth Selenide С C Carbon Cr Chromium Cu Copper **CB** Conduction band CVD Chemical vapour deposition D **D** Donor **DI** Deionized water DMS Dilute magnetic semiconductor **DUT** Device under test Ε EDTA Ethylene Diamine Tetra-acetic Acid **EDX** Energy dispersive x-ray Eg Energy gap F FESEM Field emission scanning electron microscopy FTO Fluorine doped tin oxide FE Field emission FL Fermi level G GaN Gallium nitride L ICDD International Center for Diffraction Data **ITO** Indium tin oxide Μ M Molarity Ν

N<sub>2</sub> Nitrogen

Ni Nickel 0 O<sub>2</sub> Oxygen Ρ PC Personal computer **PET** poly (ethylene terephthalate) **PL** Photoluminescence R **RT** Room temperature S **SEM** Scanning electron microscopy **SIMS** Secondary ion mass spectrometry Sr Strontium Т **TEM** Transmission electron microscopy **Ti** Titanium TiO<sub>2</sub> Titanium dioxide **TI** Topological Insulator U **UV** Ultraviolet V **VB** Valence band W W Watt Χ **XPS** X-Ray photoelectron spectroscopy **XRD** X-Ray diffraction XANES X-ray Absorption Near Edge Structure Ζ **ZnO** Zinc oxide

## **Physical Constants and Conversion Factors**

Avogadro's number	$N_A = 6.02 \times 10^{23} \text{ molecules/mole}$
Boltzmann's constant	$k = 1.38 \times 10^{-23} \text{ J/K}, 8.62 \times 10^{-5} \text{ eV/K}$
Electronic charge (magnitude)	$q = 1.6 \times 10^{-19} \mathrm{C}$
Electronic rest mass	$m_{\rm e} = 9.11 \times 10^{-31}  \rm kg$
Planck's constant	$h = 6.63 \times 10^{-34}$ J.s, $4.14 \times 10^{-15}$ eV.s
Speed of light	$c = 3 \times 10^8 \text{ m/s}, 3 \times 10^{10} \text{ cm/s}$

### **Prefixes:**

1 Å (angstrom) = $10^{-10}$ m	milli-, $m-=10^{-3}$
1 $\mu$ m (micron) = 10 <sup>-6</sup> m	micro-, μ- = 10 <sup>-6</sup>
$1 \text{ nm (nano)} = 10^{-9} \text{ m}$	nano-, $n-=10^{-9}$
2.54 cm = 1 in.	pico-, $p-=10^{-12}$
$1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$	kilo-, $k-=10^3$
	mega-, $M-=10^6$

# **Chapter 1**

# Introduction to Topological Insulator Material: Bismuth Selenide

This chapter starts with the elementary overview of topological insulator (TI), its fundamental properties and applications. Then the classification of TIs and their corresponding crystal structures are described. After that the chapter concentrates on Bismuth Selenide (Bi<sub>2</sub>Se<sub>3</sub>), the material of concern in this thesis. This segment comprises of a brief review on choice of material: Bi<sub>2</sub>Se<sub>3</sub>, its properties, various types of synthesis process, characterization and evolution as a material with application on diverse departments. Apart from these it covers a specific study on nanomaterials, superconductivity and humidity sensing where utmost attention is given to multifunctional applications of Bismuth Selenide.

## 1.1. Background and Motivation

The improvement of science and technology entices the exploration of the world in the field of condensed matter physics and nanomaterials. A very significant study in this area is the phase of matter and classification of different materials according to this. The rudimentary concept of Topological Insulator (TI) comes from the fact that they can't be defined or classified by general order of phases of matter like local order parameter, symmetric breaking theory and long-range correlation [1-3]. TI is a common apprehension of science because its discovery is of great worth to basic physics of semiconductor devices, quantum computing and spintronic devices.

### 1.1.1. Prelude to Topological Insulator

The preface of TI was none other than the Quantum Hall Effect (QHE) for which K.V. Klitzing won the 1985 Nobel Prize in Physics [4]. QHE is the Hall Effect under the influence of large magnetic field (~ 20T) and low temperature (~ 12K), which limits its development as it involves high cost for the generation of strong magnetic field and to maintain low temperature. So, researchers all over the world were searching for some material which is boast of having QHE in normal temperature without the application of high magnetic field. In 2005 the scientific thirst is quenched upon the discovery of Quantum Spin Hall Effect (QSHE) by some experiment, where an electronic state similar to QHE is observed in some material by the inherent nature of strong spin-orbit coupling effects rather than specific environment [5]. Here comes the TI which has the Quantum Spin Hall (QSH) states at room temperature. After that there was no looking back in the field of TI as plethora of theoretical calculations (Band inversion, Z2 topological invariant, etc.) and scientific experiments (Surface state study through Angle Resolved Photo Electron Spectroscopy (ARPES), etc.) to establish those theoretical aspects were carried out in the last decade. The

present scenario confirms well established theoretical studies but the practical application is still at an initial stage. Devices based on TI are also limited in literature survey, further industry application is still challenging.

### 1.1.2. Overview of Topological Insulator

Overall, solid materials are divided into three categories: conductor, semiconductor and insulator. A Conductor is a material which has free electrons in the bulk conduction band because of the overlapping of bulk conduction band and valence band. The free electrons can move without crossing the band gap as a result they are highly conducting. Insulators are the materials which have wide band gap between the valence band and conduction band for which they don't conduct electricity. The valence electron must get enough energy to cross the gap and transfer to conduction band which is not likely in normal condition. The band gap of a semiconductor lies in between the conductor and the insulator that's why they can conduct charge carriers when subjected to an applied bias voltage. Nonetheless, the TIs simply don't fall in any of the above categories.



**Figure 1.1.** (a) Schematic real-space picture of the 2D helical surface state of a 3D TI. (b) Energy dispersion of the spin non-degenerate surface state of a 3D TI forming a 2D Dirac cone. (c) Schematic of 1D metallic edge states wrapping along the edges of 2D TIs.

TI has bulk electronic state with narrow band gap, which means there are no free carriers inside the bulk states. However, it has metallic surface state which is topologically protected. This gapless surface state has Dirac point that can pass through the band gap, which means the surface of the TI is conductive [6]. This special surface state is formed due to its internal strong spin-orbit coupling effects and the time-reversal symmetry which means that the TI can reduce or avoid the scattering effects of non-magnetic impurities [7].

### 1.1.3. Types of Topological Insulator

Generally, TIs can be classified according to three ways which are as follows (i) Classification by Dimension

(ii) Parity of Dirac Points and (iii) Symmetry.

### 1.1.3.1. Classification by Dimension

There are two types of TI when grouped according to dimension, **2D** and **3D**. In 2D TI one dimensional edge state is the electronic state whereas for 3D TI the electronic states are the gapless surface states (2D). Which means for 3D TI, the outer surface is the topological metallic state while its bulk is the insulator. Some basic examples of the TIs are 2D: HgCdTe quantum wells, ZrTe<sub>5</sub>, HfTe<sub>5</sub>, *etc.* and 3D: Bi<sub>2</sub>Se<sub>3</sub>, Bi<sub>2</sub>Te<sub>3</sub>, Sb<sub>2</sub>Te<sub>3</sub>, *etc.* From experimental point of view 3D TI compounds are easy to prepare as compared to 2D TI because they have relatively stable stoichiometry resulting in a higher phase purity.

### **1.1.3.2.** Classification by Parity of Dirac Points

In this case, TIs are classified as (i) Weak TI and (ii) Strong TI. In case of weak TI, even number of Dirac points are present in the surface Brillouin zone. For example, Sb<sub>2</sub>Se<sub>3</sub>, where the localization of electrons takes place on the surface due to strong disorder. But for strong TIs like Bi<sub>2</sub>Se<sub>3</sub>, Bi<sub>2</sub>Te<sub>3</sub>, Sb<sub>2</sub>Te<sub>3</sub>, *etc.* the surface states have odd number of Dirac points so electron localization is unaffected by disorder on the surface, as a result the surface states are perfectly metallic.
#### 1.1.3.3 Classification by Symmetry

Different types of symmetries are associated with physics behind TI like (i) Time Reversal Symmetry (ii) Low Crystal Symmetry (iii) Lorentz Symmetry. While time reversal symmetry is followed by all of the TIs *i.e.* Bi<sub>2</sub>Se<sub>3</sub>, Bi<sub>2</sub>Te<sub>3</sub>, Sb<sub>2</sub>Te<sub>3</sub>, *etc.* Weyl semimetals (WSM) like WTe<sub>2</sub> and MoTe<sub>2</sub> have one extra symmetry in the form of low crystal symmetry. Apart from the above two symmetries TaP, NbAs, TaAs and NbP have Lorentz symmetries also.



**Figure 1.2.** (a) Schematics of the band structure of a 3D TI with surface states within the band gap. (b) Experimental ARPES results: band structure of surface states of Bi<sub>2</sub>Se<sub>3</sub> showing Dirac point.

# **1.2.** Bismuth Selenide: The Material of Interest

As already mentioned in the previous two sections, Bismuth Selenide  $(Bi_2Se_3)$  is a typical 3D strong TI which in turn is a grey compound of bismuth and selenium. It is one of the bismuth chalcogenide materials because it contains one or more chalcogen elements (*e.g.* S, Se or Te) as a substantial constituent. In chemistry sometimes it is also designated as

 $V_2VI_3$  compound as Bi is in group V and Se in group VI of the periodic table. Before the discovery of TI,  $V_2VI_3$  compounds such as Bi<sub>2</sub>Se<sub>3</sub>, Bi<sub>2</sub>Te<sub>3</sub> and Sb<sub>2</sub>Te<sub>3</sub>, *etc.* were known to the scientific community as good thermoelectric materials.

#### **1.2.1. Evolution of Bi**<sub>2</sub>Se<sub>3</sub>: Literature Survey

Bi<sub>2</sub>Se<sub>3</sub> has garnered a lot of attention for many decades with research interest growing from strength to strength. Bismuth was first discovered by French chemist Claude Geoffroy in 1753 and Selenium in 1817 by Jöns Jacob Berzelius, a Swedish chemist. Initially people used to work in other forms of selenides like Hydrogen Selenide [8], Tin Selenide [9], Strontium and Barium Selenides [10]. Strangely the first hint of Bi<sub>2</sub>Se<sub>3</sub> was in an article for nomenclature of Sulfide minerals [11] way back in 1920 where it is named as "Selenobismuthite". Crystal structure and lattice parameters of Bi<sub>2</sub>Se<sub>3</sub> were first discovered in 1953 by German scientist K. Schubert of Max-Planck Institute, Stuttgart [12]. Four years later in 1957 first single crystals of Bi<sub>2</sub>Se<sub>3</sub> were synthesized by Sylvania Electric Products, New York, USA [13]. They used the method of melting the constituent elements in stoichiometric proportions in a Bridgeman type furnace for studying the electrical and optical properties. Although there was some sort of confusion regarding the stoichiometry of the material, properties like melting point, optical energy gap, resistivity, carrier concentration, mobility of electrons and holes along with thermo-electric power (all at 300K) were measured. The values they measured were close to the standard values we use now which will be discussed later. Two years later in 1959, upon using a sensitive method of differential thermal analysis G. Offergeld, a Belgian scientist successfully determined the composition of Bi<sub>2</sub>Se<sub>3</sub> [14] with the congruent atomic compositions of Bi 40.02/Se 59.98  $\pm$  0.02. Initially thermoelectric properties of Bi2Te3 - Bi2Se3 alloys were investigated [15-17] because Bi<sub>2</sub>Te<sub>3</sub> was already established as a good thermoelectric material [18-21].

After that band structures of Bi<sub>2</sub>Se<sub>3</sub> were extensively analysed by D L Greenaway and G Harbeke [22] in 1965 by studying the fundamental reflectivity over the energy range 0.1-12 eV and the absorption over the range 0.1-1.5 eV. Galvanomagnetic effects in Bi<sub>2</sub>Se<sub>3</sub> single crystals were investigated at a low temperature of 90 K by K Hashimoto of Kyushu University [23]. In 1967, for the first time single crystals of Bi<sub>2</sub>Se<sub>3</sub> were studied by x-ray diffraction [24]. They also studied the crystal structures and determined the layer by layer pack of  $A_2X_3$  compounds in which double A<sub>2</sub> layers, connected together with covalent bonds were uniformly distributed between five-layer packs of the X-A-X-A-X type. It gives me immense pleasure to state that Indian scientists A N Vishnoi and B K Agarwal from Allahabad University reported measurements on the chemical shifts of the K-edge of selenium and Liii edges of bismuth in Bi<sub>2</sub>Se<sub>3</sub> from X-ray absorption spectra for the first time [25]. Electron diffraction study on vapor phase deposits of Bi<sub>2</sub>Se<sub>3</sub> by reflection and transmission techniques revealed rhombohedral crystal structure with hexagonal unit cell even at very high temperature of 400°C [26]. X-ray photoelectron spectroscopy (XPS) study on Bi<sub>2</sub>Se<sub>3</sub> were first carried out by Thomas P Debies and J Wayne Rabalais of University of Houston in 1977 [27]. The valence band density of states and core levels were measured with the evidence for two inequivalent selenium atoms in the spectrum of the Bi<sub>2</sub>Se<sub>3</sub> structure has been observed. The X-ray absorption study on Bi  $L_{iii}$  edges and Se K edge brings out the difference in the nature of the chemical bond of two types of selenium atoms, SeI and SeII in Bi2Se3 crystal structure (-Se<sub>I</sub> - Bi - Se<sub>II</sub> - Bi - Se<sub>I</sub> -) [28]. Scientists H Kohler and C R Becker investigated optically active lattice vibrations of Bi<sub>2</sub>Se<sub>3</sub> single crystals from the reflectivity of cleavage planes at nearly normal incidence of the radiation  $(E \perp c)$  [29]. Electronic properties such as type of charge carrier, number density of the carrier, electron mobility, etc. of melt growth Bi<sub>2</sub>Se<sub>3</sub> single crystals were measured by Hyde *et al.* by Hall, magnetoresistance and Shubnikov-de Haas measurements in 1974 [30]. Bogatyrev et al. [31]

proposed scattering mechanism of free carriers in Bi<sub>2</sub>Se<sub>3</sub> crystals where they stated the scattering by acoustic phonons prevails contributing about 75% and the scattering on ionized impurities contributes the remaining 25% with the concentration of free electron ~  $2 \times 10^{19} \text{ cm}^{-3}$ . First time thermoelectric power of Bi<sub>2</sub>Se<sub>3</sub> single crystals were measured by Middendorff et al. [32], that too also in strong transverse magnetic field to determine the saturation values of the magneto-Seebeck coefficient and Hall constant. The density of states and the chemical potential were determined as a function of electron concentration in the conduction band of Bi<sub>2</sub>Se<sub>3</sub> single crystals. In 1972, Woollam et al. [33] claimed n-type Bi<sub>2</sub>Se<sub>3</sub> single crystals grown by the Bridgman technique will make excellent Hall Effect magnetometers for cryogenic use by direct immersions of the crystal into liquid helium and liquid nitrogen for 50 times. For the first time the Raman-active lattice vibrations of Bi<sub>2</sub>Se<sub>3</sub> were investigated with Raman scattering by Richter et al. [34] and three of the four expected Raman modes  $E_g$  and  $A_{Ig}$  were determined. Magneto-resistivity  $\rho_{xx}$  and Hall resistivity  $\rho_{yx}$  were measured between 4.2 K and 300 K of both *n*- and *p*- type Bi<sub>2</sub>Se<sub>3</sub> single crystals grown by modified Bridgeman technique by Woollam et al. [35] to determine the temperature dependence of the Hall mobility ( $\mu_{\rm H}$ ), conductivity mobility  $\mu_{\rm c}$ , the electrical conductivity  $\sigma_{xx}$  and the carrier concentration. Kohler *et al.* [36] explored the conduction band Fermi surface at high electron concentrations of 4 X 10<sup>19</sup> cm<sup>-3</sup>. The effects of annealing temperature and time on Seebeck coefficient of Bi<sub>2</sub>Se<sub>3</sub> was investigated by Yokota et al. [37] also mentioning that the formation of Schottky defect in Bi2Se3 is estimated to be 0.35 eV. XPS and Ultraviolet Photoelectron Spectroscopy (UPS) measurements were carried out on crystalline as well as amorphous Bi<sub>2</sub>Se<sub>3</sub> films by Takahashi et al. which reveals that the bonding is more covalent in amorphous phase than in crystalline phase also suggesting that the Bi atoms in crystalline Bi<sub>2</sub>Se<sub>3</sub> are six-fold coordinated by Se atoms [38]. To obtain more insight into the lattice dynamics and binding of the layers of  $V^2VI^3$ semiconducting compounds, the generalised phonon density of states  $G(\omega)$ 

has been determined by Rauh et al. [39] by means of inelastic neutron scattering from powder samples of Bi<sub>2</sub>Se<sub>3</sub> and the results indicate that the corresponding lattice modes consist predominantly of group VI element motion. In 1982, Thuler et al. of Northern Illinois University measured the valence band density of states and the binding energies of the weakly bound core levels of Bi<sub>2</sub>Se<sub>3</sub> by XUV photoelectron spectroscopy using synchrotron radiation [40]. Chemical shifts of the Bi 5d and Se 3d levels were determined indicating partial ionicity of the mainly covalent bonds involved. For the first time a distinct anisotropy of electrical resistivity, thermopower and plasma reflectivity along perpendicular and parallel to the trigonal c axis were observed in Bi<sub>2</sub>Se<sub>3</sub> single crystals by Stordeur *et al.* [41] but they also found that Hall effect is isotropic. Wang et al. [42] in 1998 synthesized nanocrystalline Bi<sub>2</sub>Se<sub>3</sub> by a novel solvothermal method at low temperature using BiCl<sub>3</sub>, Se powder and Sodium Iodide (NaI) as reagents, getting a shape in the form of spherical grains with an average size of 25 nm. Later that year they used Potassium Borohydride (KBH<sub>4</sub>) instead of NaI to obtain  $Bi_2Se_3$  nanorods with average size of 60 nm x 1.0  $\mu$ m [43]. Thin films of Bi<sub>2</sub>Se<sub>3</sub> were prepared using chemical deposition by Nkum et al. [44] where optical absorption measurement and resistance measurement revealed the band gap energy of 1.42 eV and activation energy of 0.31 eV, respectively.

#### 1.2.2. Literatures on Doping

As the materials discussed in the working part of the thesis are transition metal doped Bi<sub>2</sub>Se<sub>3</sub> which has been used to study the effect of the doped material on the properties of Bi<sub>2</sub>Se<sub>3</sub>, a brief literature survey on doping of Bi<sub>2</sub>Se<sub>3</sub> is discussed. Copper doped Bi<sub>2</sub>Se<sub>3</sub> was first reported by Vasko *et al.* [45] in 1974 where presence of possible point defects are introduced by Cu atoms into the Bi<sub>2</sub>Se<sub>3</sub> lattice leads to the conclusion that in Cu doped Bi<sub>2</sub>Se<sub>3</sub> crystals Cu exist in the form of singly ionized interstitial atoms Cu<sub>i</sub><sup>+</sup> which act as donors. For the first time Bi<sub>2</sub>Se<sub>3</sub> was subjected to intercalation was in

1988 when Paraskevopoulos et al. used chemical treatment to insert Lithium into  $Bi_2Se_3$ , introducing additional layers perpendicular to the c axis, with a periodicity of about 60Å, as has been revealed by transmission electron studies [46]. Later Cu was intercalated into the Bi<sub>2</sub>Se<sub>3</sub> single crystals in 1997 by Kyratsi et al. [47] where Hall effect and resistivity measurements reveal that the inserted Cu is acting as a donor, enhancing the *n*-type character of  $Bi_2Se_3$ . Indium doped  $Bi_{2-x}In_xSe_3$  single crystals showed that the free electron concentration increases up to x = 0.1 then decreases where the interaction of In atoms with the already present anti-site defects in the lattice leads to the formation of uncharged but positively polarized point defects  $In_{Bi}^{(\delta^+)}$  [48] unlike Tin (Sn) doped Bi<sub>2</sub>Se<sub>3</sub> where incorporation of Sn atoms decrease the electron concentration because the defects are created due to the substitution of Bi atoms by Sn atoms act as acceptors [49]. The introduction of Cadmium (Cd) atoms into Bi<sub>2</sub>Se<sub>3</sub> crystal results in Cd atoms occupy the sites of Bi atoms thus creating Cd<sub>Bi</sub> defects of acceptor nature which decreases the electron concentration than pure Bi<sub>2</sub>Se<sub>3</sub> [50]. Doping of Lead (Pb) into Bi<sub>2</sub>Se<sub>3</sub> lattice structure results in Pb atoms having an interaction with Se vacancies and BiSe antisite defects thus increasing the free charge carrier concentration when the Pb impurities are at low concentration [51], also when the impurity concentration is high the charge carrier concentration decreases. Karamazov et al. [52] determined that the increasing content of Pb atoms in the Bi<sub>2</sub>Se<sub>3</sub> lattice leads to a suppression of the role of the mechanism of scattering by ionised impurities; at higher concentrations of Pb in the crystal the mechanism of scattering of free carriers by acoustic phonons becomes dominant. Magnetic impurity was introduced in Bi<sub>2</sub>Se<sub>3</sub> lattice in 1997 when Iron-doped Bi<sub>2</sub>Se<sub>3</sub> single crystals were prepared by a modified Bridgman method [53]. Characterization of the samples by measuring the reflectivity, optical transmission, electrical conductivity, Hall and Seebeck coefficients ascribed to the presence of point defects formed by ionized iron atoms entering interstitial positions in the Bi<sub>2</sub>Se<sub>3</sub> crystal lattice which results in an increment of the free electron

concentration [53]. The energy band structure of single crystals of *n*-type  $Bi_{2-x}Sb_xSe_3$  was investigated by Kulbachinskii *et al.* [54, 55] by cyclotron resonance in high magnetic fields up to 150 Tesla where two resonance peaks were observed corresponding to two conduction bands. The substitution of Se atoms by As atoms in the  $Bi_2Se_3$  lattice, *i.e.* formation of  $Bi_2Se_{3-x}As_x$  results in a decrease in the free electrons concentration which is probably associated with the formation of Se atoms [56].



**Figure 1.3** (a) Schematic diagram of crystal structure of layered Bi<sub>2</sub>Se<sub>3</sub> showing quintuple layer. (b) Schematic diagram showing Cu intercalation in the van der Waals gap.

#### 1.2.3. Crystal structure of Bi<sub>2</sub>Se<sub>3</sub>

Bismuth Selenide is a  $V_2VI_3$  compound having tetradymite structure. The name tetradymite denotes to the mineral Bi<sub>2</sub>Te<sub>2</sub>S which basically has the same crystal structure as the compounds Bi<sub>2</sub>Te<sub>3</sub>, Bi<sub>2</sub>Se<sub>3</sub>, Sb<sub>2</sub>Te<sub>3</sub> and some mixed compounds. The crystal structure is trigonal with space group  $D_{3d}^5$ -

R(-3)m (Space Group No. 166). The atomic arrangement in  $Bi_2Se_3$  can be visualized in terms of the layer structure. Here each sandwich (One  $Bi_2Se_3$ ) is built up by five monoatomic sheets with the sequence  $-Se_1-Bi-Se_2-Bi Se_1--Se_1-Bi-Se_2-Bi-Se_1-$  where 1 and 2 denote two different chemical states for the anions. The anions  $Se_2$  forming the middle atomic sheets are nearly octahedrally coordinated to six metal atoms. The outmost chalcogen atoms  $Se_1$  are strongly bound to only three metal atoms of the same sandwich and weakly bound to three  $Se_1$  atoms of the next sandwich which corresponds to the easy cleavage between adjacent  $Se_1$  layers. The bond lengths and bond angles of different types in  $Bi_2Se_3$  are shown in the following table [57]. The interlayer distance is much smaller than the van der Waals distance.

Table 1.1. The bond lengths and bond angles of Bi<sub>2</sub>Se<sub>3</sub>

Bond Le	nd Length (Å) Bond Angles (°)				
Bi–Se <sub>1</sub>	Bi–Se <sub>2</sub>	Se <sub>1</sub> –Se <sub>1</sub>	Se <sub>1</sub> -Bi-Se <sub>1</sub>	Se <sub>2</sub> –Bi–Se <sub>2</sub>	Se <sub>1</sub> -Se <sub>1</sub> -Se <sub>1</sub>
2.97	3.04	3.27	88.1	84.9	78.3

The lattice parameters '*a*' and '*c*' are of 4.143 Å and 28.636 Å, respectively [57]. In addition to intrinsic material properties, the lattice parameters are affected by extrinsic properties the concentration of impurities with different ionic radii which can replace the host atom as well as intercalate in the van der Waals gap, substrate and impurity induced strain along with temperature. Structural phase transitions is observed in Bi<sub>2</sub>Se<sub>3</sub> when subjected to high pressure by Yu *et al.* [58] where ambient rhombohedra phase transforms to monoclinic phase and eventually to a high pressure body-centred tetragonal phase.

## 1.2.4. Physical properties of Bi<sub>2</sub>Se<sub>3</sub>

Physical properties are used to observe and describe a material. The wellknown physical properties of Bi<sub>2</sub>Se<sub>3</sub> are listed in the following table.

Property	Value
Molecular formula	Bi <sub>2</sub> Se <sub>3</sub>
Molecular Weight	654.874 g/mol
Appearance	Dull Grey Powder
Stable phase a 300 K	Tetradymite
Density	6.82 g/cm <sup>3</sup>
Melting Point	710°C
Boiling Point	2360°C
Solubility in water	Insoluble
Thermal Conductivity	0.025 W cm <sup>-1</sup> K <sup>-1</sup> at 300K
Refractive Index	3.88
Lattice Constants	$a_0 = 4.143$ Å, $c_0 = 28.636$ Å
Relative Dielectric Constant	~ 29
Band Gap	0.3 eV, Direct
Intrinsic Carrier Concentration	< 10 <sup>19</sup> /cc
Exciton Binding Energy	0.08 eV
Carrier mobility (at 300 K)	$30 \text{ cm}^2/\text{V/s}.$

Table 1.2. Physical properties of Bi<sub>2</sub>Se<sub>3</sub>.

## 1.3. Synthesis Techniques of Bi<sub>2</sub>Se<sub>3</sub>

As mentioned above,  $Bi_2Se_3$  is a good functional material with plethora of applications and properties. The method of preparation is important as different methods give rise to different structures and morphologies with diverse research and applications. Various methods like solid state reaction, chemical synthesis, *etc.* have been used over the ages to synthesize single as well as polycrystals, nanostructures, thin films, *etc.* and are thoroughly listed in the following table. We have used modified melt growth method to make good quality single crystals and standard hydrothermal method (sometimes solvothermal method) to produce nanoparticles of pure  $Bi_2Se_3$  and doped  $Bi_2Se_3$  materials which is described in the next chapter of the dissertation.

Method	Precursors	Conditions	Properties	Ref.
		Pellets placed	1	
Melt Growth Method	Bi and Se powders, then pressed into pellets	in quartz tube, Pressure: 10 <sup>-3</sup> Pa, 850°C slowly cooled to 620°C	Single crystals with Shiny mirror like surfaces	[59]
Successive Ionic Layer Adsorption and Reaction (SILAR)	FTO coated glass substrate. Bi(NO <sub>3</sub> ) <sub>3</sub> Na <sub>2</sub> SeSO <sub>3</sub>	Immersion of substrate in cationic and anionic precursor solutions for 50s at room temperature (RT)	Thin film of 0.92 µm thick consisting of nanoparticles	[60]
Hydro- thermal Reaction	Ti foil, Bi(NO <sub>3</sub> ) <sub>3</sub> Na <sub>2</sub> SeO <sub>3</sub> NaBH <sub>4</sub> , (CH <sub>3</sub> ) <sub>4</sub> N(O H) solution	Autoclave: 170°C for 2 days, Washed in DI water, dry in air	Thin films of nanoribbons: width of 220 nm and thickness of 50 nm	[61]
Pulsed Laser Deposition	SrTiO <sub>3</sub> substrate with polycrystalli ne BioSea	Base pressure 0.4 mPa, Substrate temperature (T <sub>s</sub> ):120°C, 350 °C	Film thickness: 30 to 1200 nm, Amorphous films	[62]
	target	Base Pressure 0.3 mbar, T <sub>s</sub> :290°C	Film thickness: 10 to 20 nm	[63]

Table 1.3. List of different synthesis techniques of  $Bi_2Se_3$ .

Pulsed Laser Deposition	Si Substrate: (100) oriented with Bi <sub>2</sub> Se <sub>3</sub> alloy target	Pressure $3X10^{-3}$ Pa, T <sub>s</sub> : RT to 400°C	100 nm thick film of hexagonal crystal structure	[64]
Melt Growth Method followed by	Bi and Se segments to form Bi <sub>2</sub> Se <sub>3</sub> alloys Nonconduct ive glass substrate	10 <sup>-5</sup> Torr, 1000°C Annealed 250 and 300 °C for 3 hrs	Polycrystalli ne single phase particle size:700nm, Film thickness 200nm	[65]
Thermal Evaporation	Same segments with Si (100) substrates	<ul> <li>10<sup>-3</sup> Pa, 850°C</li> <li>slowly cooled</li> <li>to 620°C</li> <li>Annealed 200-</li> <li>480°C, Se rich</li> <li>environment</li> </ul>	Rhombohedr al layered crystal structure Film thickness 300nm	[66]
Electro- deposition	Si, Ru and Au substrates, Bi(NO <sub>3</sub> ) <sub>3</sub> , SeO <sub>2</sub>	pH: 0.2-0.4 Applied Potential vs SCE: -0.5V for Si -0.1V for Au 0.2V for Ru	Hemispheric al islands coalesced together forming Platelet morphology	[67]
Magnetron Sputtering	Si (100) substrate, Bi <sub>2</sub> Se <sub>3</sub> alloy target	Base pressure < 2 X 10 <sup>-4</sup> Pa T <sub>s</sub> : 220°C	Film Thickness: 30 to 300 nm Hexagonal and triangle Nanoplates, Edge length 200nm	[68]

Hydrotherma l Method	Bi(NO <sub>3</sub> ) <sub>3</sub> , 5H <sub>2</sub> O Se powder DMF NaOH	Teflon lined Autoclave: 200 °C, 24hr Dried 60 °C	Rhombohedr al crystal Orientation: (015) direction	
followed by Electron Beam Evaporation	Bi <sub>2</sub> Se <sub>3</sub> pellets (12 X 2 mm <sup>2</sup> )	T <sub>s</sub> : RT, 150°C, 250°C, 350°C and 450°C Pressure 5 X 10 <sup>-5</sup> Torr	Thin Film: Poly- crystalline Hexagonal structure Thickness: 32-46 nm	[69]
Hydro- thermal Reaction	Bi and Se powder	Autoclave: 180-240°C, 10hr	Plate-like particles with width ~ 1μm thickness ~ 0.2 μm	[70]
Chemical Vapour Deposition (CVD)	Bi <sub>2</sub> Se <sub>3</sub> and Se powder, Si(111) substrate, 10 nm Au seed layer	Base pressure: 10 Pa, Ar gas atmosphere, Hot Centre: 550°C, 15 min	asymmetric, elongated hexagonal morphology with a multi- layered structure	[71]
Physical Vapour Deposition (PVD)	Bi <sub>2</sub> Se <sub>3</sub> powder, mica and Si (100) and (111) substrates, Au (Catalyst)	high vacuum (~10 <sup>-6</sup> Pa) 550°C, 30 min Ar atmosphere	Nanoribbons and nanorods with [001] crystallo- graphic orientation	[72]
Electro- deposition	Pt Sheet, SCE, ITO- coated glass substrate, Bi(NO <sub>3</sub> ) <sub>3</sub> ,	Counter electrode (CE): Pt Sheet, Reference Electrode (RE)	Net like, Cauliflower like Morphology consist of	[73]

	SeO <sub>2</sub> ,	- SCE,	numberless	
	HNO <sub>3</sub>	Working	thin sheets	
		Electrode		
		(WE) - ITO-		
		coated glass		
		substrate,		
		Potential scan:		
		-1 to 1 V		
Facile Hybrid Solution Based Method	BiCl <sub>3</sub> , Bismuth Acetate, Bi(NO <sub>3</sub> ) <sub>3</sub> , Bi <sub>2</sub> (CO <sub>3</sub> )O <sub>2</sub> , NaBH <sub>4</sub> , Se powder	Reduction of selenium using NaBH4, followed by thermolysis in an alkylamine at 190-270°C	190°C: Spherical nanocrystals 270°C: Faceted nanocrystals	[74]
CVD	Bi <sub>2</sub> Se <sub>3</sub> powder,	Ar flow, Tube furnace: 700 °C, 90 min	Nanowires with length up to 50 µm	[75]
Solvo- thermal Approach	Bi(NO <sub>3</sub> ) <sub>3</sub> , 5H <sub>2</sub> O SeO2 EDTA Ethylene Glycol (EG)	Autoclave 165°C, 24h Centrifuged 3000 rpm Vacuum Dry 60°C, 4h	Non-uniform Hexagonal plate like structures	[76]
Melting followed by Hot Pressing	Bi and Se powder in quartz ampule	Furnace Heat 1073K for 12h, Vacuum hot press 563K, 300 MPa, 60min	Flake Like Grains Stripe Like Grains	[77]
Polyol Method	Bi(NO <sub>3</sub> ) <sub>3</sub> 5H <sub>2</sub> O, (Na <sub>2</sub> SeO <sub>3</sub> ), Polyvinyl Pyrrolidone (PVP), EG	Reflux Condenser 190°C, 2h Dried 60°C	Nanoplatelet Morphology of 10nm thickness Intermediate: flow-like morphology.	[78] [79]

Melt Growth Method	Bi and Se powder	850°C, 12h 620°C, 46h Quenched in Cold water.	'c' axis oriented single crystal with shiny surface	[80] [81]
Melt Growth Method	Elemental Bi and Se	850°C, 48h Slowly cooled to 620°C, 24h Quenching in cold water	Layered hexagonal crystal structure	[82]
Arrested Precipitation Technique	[Bi(NO <sub>3</sub> ) <sub>3</sub> , 5H <sub>2</sub> O], Se powder, Na <sub>2</sub> SO <sub>3</sub> , TEA,	NH <sub>3</sub> Solution to maintain pH, acacia as surfactant	Thin film, without surfactant: Interconnect ed mesh like structure, with surfactant: nanospheres	[83]
Molecular Beam Epitaxy (MBE)	Bi and Se source fluxes, Si (111) and InP (111) substrate	T <sub>s</sub> :250°C, sample heated up to 300°C, annealed for 1h	Thin film, coalesced islands of triangular shape	[84]
Pulsed Laser Deposition (PLD)	Bi <sub>2</sub> Se <sub>3</sub> alloy target, pulsed KrF excimer laser	Si wafer substrate, Ts: RT to 400°C	Hexagonal nano- structures	[85] [86]
Metal Organic Chemical Vapour Deposition (MOCVD)	Pyrex Substrate, Trimethylbi smuth (TMBi), Diethylsele nium (DESe)	Growth Temperature: 480°C, Carrier Gas: Hydrogen	Typical morphology of Bi <sub>2</sub> Se <sub>3</sub> layer: Flake like but of different sizes	[87]

Photo- chemical Reaction route	Bi(NO <sub>3</sub> ) <sub>3</sub> , 5H <sub>2</sub> O SeO2 EDTA	Mercury lamp ( $\lambda > 290$ nm), ultraviolet irradiation for 3 hr at RT.	Nanospheres and nanorods Average Size: 35 nm	[88]
Solvothermal Reaction	BiCl <sub>3</sub> , Se powder, Na <sub>2</sub> SO <sub>3</sub> , Di Ethylene Glycol (DEG)	Autoclave 160°C, 22h Filtered, Dried in Vacuum	Flake-like hexagonal Bi <sub>2</sub> Se <sub>3</sub> nanocrystals	[89]
Hydro- thermal co-reduction Method	H <sub>2</sub> SeO <sub>3</sub> , BiCl <sub>3</sub> , Hydrazine Hydrate (N <sub>2</sub> H <sub>4</sub> .H <sub>2</sub> O)	Autoclave: Heated at 150°C 180°C 200°C and 210°C Time: 24h Dried in vacuum at 60°C	Bi <sub>2</sub> Se <sub>3</sub> Nanoflakes: width: 50–500 nm thickness: 2–5 nm Bi <sub>2</sub> Se <sub>3</sub> Nanotubes: diameter: 5–10 nm, length: 80–120 nm wall thickness: 1.3 nm	[90]
Bridgman Method	Bi and Se elements in silica ampoule	Furnace Heat: 1050 K, 48 h Single Crystal Growth: same ampoule with a pulling rate of 1.3 mm h <sup>-1</sup>	Single Crystal with natural cleavage plane (0001)	[91]

Sono-electro- chemical approach	Bi(NO <sub>3</sub> ) <sub>3</sub> , 5H <sub>2</sub> O Na <sub>2</sub> SeSO <sub>3</sub> NTA	Set up: current densities: 35.4 - 53.0 mA/cm <sup>2</sup> . ultrasound pulse: 20 kHz	Bi <sub>2</sub> Se <sub>3</sub> Nanowires: diameter: 10 to 40 nm Length: 500 nm to 2 µm	[92]
Microwave- assisted polyol method	Elemental Se, Bismuth Oxynitrate (BiONO <sub>3</sub> ) EG	Spectra 900 W microwave oven, 2.45 GHz, On for 21s, Off for 9s	Nano Cucumber like shapes: length: 300 nm width: 20–80 nm	[93]
Solvothermal Approach	Bi(NO <sub>3</sub> ) <sub>3</sub> , 5H <sub>2</sub> O SeO <sub>2</sub> EDTA, EG	Uniform dispersion (sonicated for 15 min) Autoclave 165°C, 24h	Nanoplates like structure size: 300 to 800 nm	[94]
Solvothermal process with different solvents	Bi(NO <sub>3</sub> ) <sub>3</sub> , 5H <sub>2</sub> O Se powder N <sub>2</sub> H <sub>4</sub> .H <sub>2</sub> O	TEA, Ethanol, Distilled water (H <sub>2</sub> O) and mixed solvents volume ratio 1:1	Sheet like micro- structures with 50-100 nm thickness	[95]
Electro- deposition on Si (100) substrate	Bi(NO <sub>3</sub> ) <sub>3</sub> , 5H <sub>2</sub> O SeO <sub>2</sub> , HNO <sub>3</sub>	Applied potential: - 0.4 V vs. SCE	Granular morphology with grain diameters: 200-400 nm.	[96]
MBE on Ge(111) substrate	Bi, Se source in BN crucibles	$T_{s}$ : 510K $T_{Bi}$ : 740K $T_{Se}$ : 430K Annealed: 490-530K	Single crystalline Bi2Se3 thin films	[97]

Mechanical Exfoliation followed by Lithography	n-type Bi <sub>2</sub> Se <sub>3</sub> single crystal	SiO <sub>2</sub> /Si substrates ( $\rho \sim$ 1–15 $\Omega$ cm <sup>-1</sup> )	Multilayer Bi <sub>2</sub> Se <sub>3</sub> devices	[98] [99]
Melt Growth Method	Bi, Se elements	850°C, 48h Slowly cooled to 620°C, 24h Quenching in cold water	Silvery shiny mirror like crystal easily cleavable along basal plane	[100]
Melt Growth followed by MBE	Elemental Bi, Se, Sr and SrTiO <sub>3</sub> (111) substrate	850°C, cooled to 620°C at 3°C per hour T <sub>s</sub> : 240°C during MBE	50 nm thin film with high purity	[101]
Melt growth method followed by electro- chemical synthesis	Bi, Se and Cu powders and home- made electro- chemical cell	750°C for 12h, cooled to 620°C at 3°C/hr, I ~ 10μA in electro- chemical intercalation	High purity Single crystals with Copper intercalation	[102]
Bridgman Method	Bi, Se, Cu powders (5N)	850°C for 12h, Cooled to 620°C at 3°C/hr	Crystals with metallic appearance on the surface	[103]

# 1.4. Applications of Bi<sub>2</sub>Se<sub>3</sub>

As mentioned earlier  $Bi_2Se_3$  (a  $V_2VI_3$  compound) is generally known for thermoelectric applications from very first stage. First alloys of  $Bi_2Te_3$ - $Bi_2Se_3$  were used as thermoelectric refrigeration [15-17]. After that different structures of pure  $Bi_2Se_3$  [22, 90, 104-107] were studied as thermoelectric material with also the doped ones [77, 108-112] to improve the thermoelectric properties. As a novel idea Bi<sub>2</sub>Se<sub>3</sub> rectangular nanosheets with thicknesses of 200-500 nm were used in lithium ion batteries to improve the efficiency [113]. Han et al. used Indium doped Bi<sub>2</sub>Se<sub>3</sub> nanostructures as anode materials for Li ion batteries resulted in better discharge capacity, improved cycle stability and rate performance [114]. Jin et al. [115] attained the improved performance with nanocomposites of CNT@C@Bi<sub>2</sub>Se<sub>3</sub> whereas Chen *et al.* [116] achieved that with a flexible Bi<sub>2</sub>Se<sub>3</sub>/Graphene (BSG) composite paper. The photoresponse properties of Bi<sub>2</sub>Se<sub>3</sub> nanosheets were studied by Zang *et al.* [117] with an effective use in high performance photodetectors. Nanowires [118] and 2D nanoflakes [119] of Bi<sub>2</sub>Se<sub>3</sub> were also reported to be visible as well as infrared photodetectors so as Bi<sub>2</sub>Se<sub>3</sub>/Silicon heterostructures which were reported to be broadband photodetectors [120, 121]. Das et al. [122] fabricated  $Bi_2Se_3/Si$ -nanowire based *p*-*n* junction diode for efficient near-infrared photodetector. Photoelectric properties of Bi<sub>2</sub>Se<sub>3</sub> nanoribbons film were first investigated by Yu et al. [123], then nanostructured Bi<sub>2</sub>Se<sub>3</sub> thin films were synthesized for photoelectrochemical application [124] and solar cell applications [125]. Bi<sub>2</sub>Se<sub>3</sub> is used in detection of glucose in human blood serum [126] as well and also has application for the direct electrochemistry of haemoglobin and  $H_2O_2$  detection [127]. As  $Bi_2Se_3$  is a 3D TI, it has high band velocity and high mobility at room temperature due to topologically protected surface states. These unique properties are exploited by scientists to fabricate field effect transistors from Bi<sub>2</sub>Se<sub>3</sub> thin films [128-131] as well as single crystals [99, 132, 133] and nanostructures [134-136]. Bi<sub>2</sub>Se<sub>3</sub> has also been investigated for photocatalytic properties and turned out to be a good photocatalyst in pure form [137, 138] and with better performance when doped with certain material [94, 139, 140] as well as composites [141]. Other applications of Bi<sub>2</sub>Se<sub>3</sub> include field emitters [142-144], quantum oscillators [145], spintronic devices [146, 147], ultrafast terahertz transmitter [148], sensor [149], resistive switching [150] and many more.

## **1.5.** Superconductivity

Superconductivity is a phenomenon in which the electrical resistivity of an element or a compound suddenly drops to zero (or becomes immeasurably small) at a certain temperature known as the superconducting transition temperature  $T_c$ . It was first discovered (rather accidentally) by Kamerlingh Onnes in 1911 in mercury (Hg) [151]. Since then many metallic elements like Al, Sn, Pb, Nb, *etc.* as well as intermetallic compounds such as Nb<sub>3</sub>Sn, MgB<sub>2</sub>, LaBaCuO, SrFFeAs, *etc.* have been discovered as superconducting. Unlike other phenomenon it is not correlated to periodic table such as atomic number, atomic weight, electronegativity, ionization potential, *etc.* One should also remind that like atomic spectral lines and ferromagnetism, superconductivity is a quantum mechanical phenomenon. There are mainly three hallmarks of superconductivity: 1) Zero DC Resistance 2) Complete diamagnetism and 3) Macroscopic Quantum Effects.

#### 1.5.1. Zero DC Resistance

The dc electrical resistance of certain elements and compounds disappears completely in a small temperature range at a critical temperature  $T_c$ , which is a characteristic of the material. This whole loss of resistance is most understandingly validated by experiments with persistent currents in rings of superconducting material. Once it is set up, no detectable decrease has been witnessed in such currents to flow without for a year. Thus almost perfect conductivity is the first hallmark of superconductivity. This property is used in high current transmission lines or high field magnets.

#### 1.5.2. Complete Diamagnetism

In 1933 this property was first discovered by Meissner and Ochsenfeld [152] where they found that not only a magnetic field is excluded from entering a superconductor, which can be explained by perfect conductivity but also a field in an originally normal sample is expelled as it is cooled

through  $T_c$  which means the material attains perfect diamagnetism below  $T_c$ . This effect is known as Meissner effect.

#### 1.5.3. Macroscopic Quantum Effects.

This is related to the magnetic flux structures in superconductor. Consider a superconductive ring. Assume that a magnetic field is applied at  $T > T_c$ , then the magnetic flux lines  $\Phi_0$  produced by the external field pass through and penetrate into the body of the ring. We now lower the temperature to a value below  $T_c$ , and then remove the external magnetic field. The magnetic induction inside the body of circular ring equals zero because the ring is in the superconductive state and the magnetic field produced by the superconductive current cancels the magnetic field, which was within the ring. However, part of the magnetic fluxes in the hole of the ring remain because the induced current is in the ring vanishes. This residual magnetic flux is referred to as "the frozen magnetic flux". It has been observed experimentally, that the frozen magnetic flux is discrete, or quantized. By using the macroscopic quantum wave function in the theory of superconductivity, it can be shown that the magnetic flux is established by  $\Phi' = n\Phi_0$  (n=0,1,2,...), where  $\Phi_0 = hc/2e = 2.07 \times 10^{-15}$  Wb is the flux quantum, representing the flux of one magnetic flux line. This means that the magnetic fluxes passing through the hole of the ring can only be multiples of  $\Phi_0$  [153-156]. In other words, the magnetic field lines are discrete.

### 1.5.4. BCS Theory of Superconductivity

In 1957, Bardeen, Cooper, and Schrieffer proposed [157] a quantum theory of superconductivity (the BCS theory), for which they received a Nobel Prize. Their theory in nonmathematical terms can be summarized as follows:

(a) An attractive interaction between electrons through electron-latticeelectron interaction can lead to a ground state separated from excited states by an energy gap. (b) The magnetic flux penetration depth and coherence length emerge as a consequence of the theory.

(c) Predicts a relationship between superconducting temperature,  $T_c$ , the lattice vibration,  $\theta_{\text{Debye}}$ , and average atomic mass, M, as  $T_c \propto \theta_{\text{Debye}} \propto M^{1/2}$  such that  $M^{\alpha}T_c = \text{constant}$ . Since M is an average atomic mass, it is also known as the "Isotope" effect.

(d) The criterion for the transition temperature,  $T_c$ , of an element is related to the electron density of orbital D ( $\varepsilon_F$ ) at the Fermi surface and the electronlattice interaction U, which can be estimated from the electrical resistivity. For UD ( $\varepsilon_F$ )  $\ll$  1, the BCS theory predicts  $T_c = 1.14\theta \exp \left[-1/\text{UD} (\varepsilon_F)\right]$ .

(e) Magnetic flux through a superconducting ring is quantized and the effective unit of charge is 2e. The BCS ground state predicts paired electrons, which are derived from quasifree electrons.

Some 46 years from the time the BCS theory was proposed, a large number of experimental evidence on superconductivity has accumulated. But, they do not seem to support the theory. Some obvious paradox is: experimentally, the higher the resistivity at room temperature, the more likely that metal will be a superconductor when cooled. This directly contradicts the BCS's idea that paired electrons originate from Fermi electrons. Further, if paired electrons (boson) indeed come from Fermi electrons (fermion), it would be a "boson condensation". The boson condensation temperature calculated for metallic electron concentration is of the order of the Fermi temperature of  $10^4$ – $10^5$  K. Since the superconducting transition temperatures are much lower, any electron pair is expected to break up into fermions, not forming a pair. The proposal of the Cooper electron pair is justified solely on the mathematical argument that although the kinetic energy may be high, their potential energy is lowered to the extent that they become stable; and, requiring the momentum vector for two electrons to be opposite to one another, i.e.  $+k\uparrow$  and  $-k\downarrow$ . The physical interpretation is that the two electrons in the pair should be running away from one another in the sea of other free electrons. In the "isotope" effect,  $\alpha$  parameter was predicted to be around ½. However, in experiments this value not only varies widely, ( $\alpha$ =0 for Zr and  $\alpha$ =0.61 for Tl) but in some cases the parameter is found to be negative.

## 1.5.5. Classification of Superconductors

There are mainly three criteria by which superconductors are classified

#### 1.5.5.1. Response to an external magnetic field

**Type I:** The superconductor has a single critical field, above which all superconductivity is lost and below which the magnetic field is completely expelled from the superconductor.

**Type II:** It has two critical fields; between which it allows partial penetration of the magnetic field through isolated points. These points are called vortices.

#### 1.5.5.2. Theory of Operation

**Conventional:** If the superconductor can be explained by BCS theory.

Unconventional: If it cannot be explained by BCS theory.

#### 1.5.5.3. Critical Temperature

**High Temperature:** If the material reaches a superconducting state above a temperature of 30 K. Examples: YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>, FeSe, *etc*.

**Low Temperature:** If the material has  $T_c$  below 30 K like CeCu<sub>2</sub>Si<sub>2</sub>, LaOFeAs, *etc*.

## 1.5.6. Applications of Superconductors

There are many applications of Superconductors in modern world. Magnetic-levitation is an application where superconductors perform extremely well. Transport vehicles such as trains can be made to "float" on strong superconducting magnets, virtually eliminating friction between the train and its tracks. By impinging a strong superconductor-derived magnetic field into the body, hydrogen atoms that exist in the body's water and fat molecules are forced to accept energy from the magnetic field. They then release this energy at a frequency that can be detected and displayed graphically by a computer. Superconducting magnets are frequently used in particle physics applications, anything that needs to steer the paths of charged particles. A fairly ubiquitous but less known application of superconductors is in filters for wireless communication base stations. When incorporated properly into a circuit, the zero resistance of a superconductor can select a specific bandwidth with a sharp cut-off or select a specific frequency with high specificity. A few are enlisted below:

1) Power transmission cables.

2) Fault current limiters.

3) Superconducting magnets including MRI and research magnets.

4) SQUID (Superconducting Quantum Interference Device) – Strong and sensitive sensors to detect very small magnitude of magnetic field.

5) Shielding of magnetic fields.

6) Superconducting electronics and quantum computers.

7) SMES (superconducting magnetic energy storage).

# 1.6. Humidity Sensing

Humidity sensors are widespread in many industrial applications, ranging from environmental and meteorological monitoring, soil water content determination in agriculture, air conditioning systems, food quality monitoring, and medical equipment to many other fields. Thus, an accurate and reliable measurement of water content in different environments and materials is of paramount importance. Humidity sensors are largely used in many fields where accurate and reliable measurements of water content in different environments and materials are of paramount importance. These sensors can also constitute a cheap alternative to a laboratory's analytical technique, so moisture (the water content of any material) sensors and humidity (the water vapor content in gases) sensors are used in many different areas of human activity, such as food quality monitoring, conditioning systems, meteorology, agriculture, manufacturing and process control, medical equipment, and so forth [158]. When air is fully saturated with water, the pressure exerted by the contained water vapor is defined as the saturation water vapor pressure (Ps) that is dependent on the temperature. Thus, the ratio of the current water vapor pressure to the saturation water vapor pressure at a specific temperature is a common way to quantify the amount of water vapor contained in the air [158], and it represents the relative humidity (RH). The sensor's response is often determined as the relative changes in a measured physical parameter like the impedance (Z), resistance (R), current (I), conductance (G), capacitance (C), power gain, or resonant frequency  $(f_0)$  value of the device with respect to time. Different conventions have been applied for plotting these measurements:  $\Delta X/X_0$ ,  $X/X_0$  or simply  $\Delta X$  (where X = Z, R, I, G, C, f<sub>0</sub> or power gain) [159]. Materials that show a resistivity decrease are classified as *n*-type semiconductors, while *p*-types are those presenting an increase of the resistivity when the relative humidity rises. In fact, humidity usually exhibits reducing characteristics. The requirements for effective humidity sensors that change impedance after exposure to humidity in view of practical applications are the following: good sensitivity (*i.e.*, the capability to discriminate small differences in concentration of the analyte over a wide range of RH values), a short response time (the time that a sensor needs to reach usually 90 % of the total impedance or capacitance change during adsorption of gas) and recovery time (the time taken for a sensor to achieve usually 90 % of the total impedance or capacitance change in the case of gas desorption), good reproducibility (small standard deviation in sensor response of devices realized with the same material), great repeatability (small standard deviation in sensor response of the same device under a

definite humidity concentration), very small hysteresis (the difference between the impedance value during adsorption and desorption cycles for the same RH value), negligible temperature dependence, low cost of fabrication and maintenance, resistance to contaminants, a linear response, an easy fabrication process and durability [158]. Finally, a low weight and compatibility with a microprocessor are also required features for some specific applications (*e.g.*, portable devices) [158].

## **1.7.** Nanomaterials

Technology in the twenty first century requires the miniaturization of devices in to nanometre sizes while their ultimate performance is dramatically enhanced. This raises many issues regarding new materials for achieving specific functionality and selectivity. Nanotechnology is the design, fabrication and application of nanostructures or nanomaterials and the fundamental understanding of the relationships between physical properties or phenomena and material dimensions. Nanomaterials are the particles (crystalline or amorphous) of organic or inorganic materials having sizes in the range of 1-100 nm [160]. Nanomaterials are classified into nanostructured materials and nanophase/nanoparticle materials. The former refer to condensed bulk materials that are made of grains with grain sizes in the nanometre size range while the latter are usually the dispersive nanoparticles [161]. Nanomaterials have properties that are significantly different and considerably improved relative to those of their coarsergrained counterparts. The property changes result from their small grain sizes, the large percentage of their atoms in large grain boundary environments and the interaction between the grains. It is seen that properties of these particles are quite sensitive to their sizes [162]. This is partly connected with the fact that surface to volume ratio changes with a change in particle size. A high percentage of surface atoms introduce many size-dependent phenomena. High surface area is an important feature of nanosized and nanoporous materials, which can be exploited in many

potential industrial applications, such as separation science and catalytic processing, because of the enhanced chemical reactivity [163, 164]. Depending on the dimension in which the size effect on the resultant property becomes apparent, the nanomaterials can be classified as zero dimensional (quantum dots) in which the movement of electrons is confined in all three dimensions, one-dimensional (quantum wires) in which the electrons can only move freely in the X-direction, two-dimensional (thin films) in which case the free electron can move in the X-Y plane, or three dimensional (nanostructured material built of nanoparticles as building blocks) in which the free electrons can move in the X, Y and Z directions [165].

#### 1.7.1. Applications of Nanomaterials

Since nanomaterials possess unique, beneficial chemical, physical, and mechanical properties, they can be used for a wide variety of applications. **Low-Cost Efficient Flat-Panel Displays:** By synthesising nanocrystalline phosphors, the resolution of the display devices is greatly enhanced and the manufacturing costs can be significantly reduced. Also, the flat-panel displays constructed out of nanomaterials possess much higher brightness and contrast than the conventional ones.

**High Energy Density Batteries:** Nanocrystalline materials synthesised by sol-gel techniques are candidates for separator plates in batteries because of their foam-like (aerogel) structure, which can hold considerably more energy than their conventional counterparts.

**Next-Generation Computer Chips:** The microelectronics industry has been emphasising miniaturisation, whereby the circuits, such as transistors, resistors, and capacitors, are reduced in size. Nanomaterials help the industry by providing nanocrystalline starting materials, ultra-high purity materials, materials with better thermal conductivity and long-lasting durable interconnections. **Longer-Lasting Medical Implants:** Nanocrystalline silicon carbide (SiC) is a candidate material for artificial heart valves primarily due to its low weight, high strength, extreme hardness, wear resistance, inertness (SiC does not react with biological fluids), and corrosion resistance.

**High-Power Magnets:** The strength of a magnet is measured in terms of coercivity and saturation magnetisation values. These values increase with a decrease in the grain size and an increase in the specific surface area (surface area per unit volume of the grains) of the grains which is fulfilled by nanomaterials like Y-Sm-Co grains possess very unusual magnetic properties due to their extremely large surface area.

**High-Sensitivity Sensors:** Sensors employ their sensitivity to the changes in various parameters which include electrical resistivity, chemical activity, magnetic permeability, thermal conductivity and capacitance. All of these parameters depend greatly on the microstructure (grain size) of the materials employed in the sensors. Sensors made with nanocrystalline materials are extremely sensitive to the change in their environment. Typical applications for sensors made out of nanocrystalline materials are smoke detectors, ice detectors on aircraft wings, automobile engine performance sensor, *etc*.

There are many other applications include better future weapons platform, large electrochromic display devices, aerospace components with enhanced performance, smart cutting tools etc.

## **1.8.** Scope and Goals of thesis

The main aspiration of this thesis is to synthesize different structures of Bi<sub>2</sub>Se<sub>3</sub> which are functional in its unique way contributing to the diverse fields of applications. The preliminary idea is to prepare single crystals and nanomaterials of Bi<sub>2</sub>Se<sub>3</sub> and then systematically study the modifications in their properties with transition metal (Cu, Ni) doping. The prepared single crystals and nanostructures are then implemented in diverse applications including sensing, superconductivity and field emission studies.

#### 1.8.1. Thesis Objectives

The precise objectives of the research work plans are categorised as follows:

1. Synthesis of Bi<sub>2</sub>Se<sub>3</sub> single crystals through an efficient two-step melt growth method.

2. Controlled growth of hierarchical Bi<sub>2</sub>Se<sub>3</sub> nanomaterials using simple and economical hydrothermal method.

3. Effect of transition metal (Ni and Cu) doping on Bi<sub>2</sub>Se<sub>3</sub> single crystals and nanomaterials and to study their structural, electrical and magnetic properties.

4. Exploring the doped materials for multifunctional applications: Cu intercalated Bi<sub>2</sub>Se<sub>3</sub> single crystal as humidity sensor and Ni doped Bi<sub>2</sub>Se<sub>3</sub> nanomaterials as field electron emitter.

#### 1.8.2. Thesis Outline

Greatly fortified by the overhead background, this precise exertion makes an attempt to rediscover the multifunctional applications of different structures (Single Crystals and Nanomaterials) of Bismuth Selenide, one of the widely known 3D Topological Insulator.

This work has been divided into six chapters circumscribed between the introduction chapter 1 and the conclusion and future scope of chapter 6. The chapter wise organization is summarized as follows:

#### Chapter wise organization of the thesis:

**Chapter 1: "Introduction":** This chapter primarily discusses the brief overview on the generation of physics behind topological insulator, then gradual discovery of more physics and related application. After that how Bi<sub>2</sub>Se<sub>3</sub> emerged as topological insulator and why it is fascinating to work on this material.

**Chapter 2: "Experimental Techniques and Sample Characterization":** This chapter's main objective is to present the synthesis methodologies, adopted materials synthesis techniques and characterization techniques which are used in this thesis.

**Chapter 3: "Electrical and magnetic properties of copper intercalated topological insulator Bi<sub>2</sub>Se<sub>3</sub> single crystal": This chapter essentially discuss about the basic electrical and magnetic property of Cu intercalated Bi<sub>2</sub>Se<sub>3</sub> Single Crystal and explores its superconducting nature with a brief touch on antiferromagnetic correlation.** 

**Chapter 4: "Effect of Cu intercalation on humidity sensing properties of Bi<sub>2</sub>Se<sub>3</sub> topological insulator single crystals":** The main motto of this chapter is to investigate the humidity sensing property of Bi<sub>2</sub>Se<sub>3</sub> single crystal and how Cu intercalation upto a particular atomic ratio in the Bi<sub>2</sub>Se<sub>3</sub> crystal structure enhances the sensing property by decreasing the response recovery time, increasing the linearity of the device and above all magnifying its sensitivity.

**Chapter 5: "Enhanced field emission properties of Ni doped Bi<sub>2</sub>Se<sub>3</sub> Nanomaterials":** This chapter is focussed on the field emission properties of Bi<sub>2</sub>Se<sub>3</sub> and how that particular property is significantly increased by transition metal doping in the form of Nickel.

**Chapter 6: "Conclusions and Future Scopes":** This chapter summarizes the main findings of the previous chapters and also describes the probable future scope of the research work that can be undertaken in this area.

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# **Chapter 2**

# Experimental Techniques and Sample Characterization

This chapter elaborates the experimental methods employed to synthesize and characterize the single crystals of Bi<sub>2</sub>Se<sub>3</sub> and its nanostructured powder that are described in this thesis. Initially, two synthesizing methods are described briefly. Firstly, the modified two step melt growth method for the synthesis of single crystals is described. Secondly, the hydrothermal and solvothermal route that is employed for preparing Bi<sub>2</sub>Se<sub>3</sub> nanostructures are presented. Finally, a brief review of the various analytical tools including their principle of operations for material characterizations are summarized along with the measurement processes of the two applications (Field Emission and Humidity Sensing) of Bi<sub>2</sub>Se<sub>3</sub>.

# **2.1.** Synthesis of Single Crystal

Synthesis of phase pure single crystals of Cu<sub>x</sub>Bi<sub>2</sub>Se<sub>3</sub> is challenging. Schneeloch *et al.* [1] discovered that the melt growth method is much more efficient than the floating zone method for the synthesis of Cu intercalated single crystals. It was also discussed that an optimized quenching temperature above 560°C is generally an essential criterion for Cu<sub>x</sub>Bi<sub>2</sub>Se<sub>3</sub> to achieve superconductivity. A reproducible process of synthesis was discussed by Kondo et al. [2] who used an improved two step melt growth method for synthesizing high quality single crystals. High quality samples (superconducting shielding fraction of around 50 %) of Cu intercalated Bi<sub>2</sub>Se<sub>3</sub> were electrochemically synthesized by Kreiner *et al* [3]. Wang *et al*. [4] also discussed the synthesis of zero resistance  $Cu_x Bi_2 Se_3$  samples by using a combined method of electrochemical intercalation and melt growth, where Cu was electrochemically intercalated in already synthesized Cu<sub>x</sub>Bi<sub>2</sub>Se<sub>3</sub> single crystals produced by melt growth method. Generally electrochemical intercalation results in enhanced charge accumulation on the surface as compared to the inner bulk, which affects the superconductivity. Thus the melt growth method is a better synthesis technique for the controlled growth of the single crystals, whereas Cu<sub>2</sub>Se, a by-product formed due to the consumption of Cu atoms during the conventional melt growth process, obstructs the intercalation of Cu in between the Bi<sub>2</sub>Se<sub>3</sub> layers [2]. Cu<sub>2</sub>Se, having a melting point of 1050°C, is generally produced during the initial synthesis steps of the melt growth process. It sublimates in the evacuated sealed ampule during further melting steps and thus restricts the growth of Cu<sub>x</sub>Bi<sub>2</sub>Se<sub>3</sub>. To overcome the above problems, here we have employed an improved two-step melt growth method for the synthesis of superconducting Cu<sub>x</sub>Bi<sub>2</sub>Se<sub>3</sub> samples by using CuSe (higher oxidized Cu-Se material) [2] as a precursor instead of  $Cu_2Se$ . During this synthesis, first we prepared the CuSe precursor having a melting point of 387°C, which is much lower than that of Bi<sub>2</sub>Se<sub>3</sub> (710°C). All the

reagents Cu (5N), Bi (5N) and Se (4N), metal basis, were of analytical grade from Sigma-Aldrich Co. Ltd., and were used without any further purification. Stoichiometric mixtures of Cu and Se (*i.e.*, 0.1:0.1 in Cu<sub>0.1</sub>Bi<sub>2</sub>Se<sub>3</sub>) were thoroughly ground and mixed in an agate mortar, pelletized in the form of circular pellets of diameter 1 cm by applying a pressure of 5 ton using a hydraulic press. The pellets were sealed in an evacuated quartz tube at a pressure of  $2.5 \times 10^{-5}$  mbar. The tube was kept overnight in a muffle furnace at 900°C followed by quenching in ice-water to avoid the production of Cu<sub>2</sub>Se. According to the equilibrium phase diagram of the Cu–Se system [5], Cu<sub>2</sub>Se is produced for all values of Cu/Se ratio. The quenching process is needed to avoid the production of Cu<sub>2</sub>Se. The absence of Cu<sub>2</sub>Se and the presence of CuSe in our sample have been confirmed by X-ray diffraction (XRD) measurements.



**Figure 2.1** (a) Heat treatment maintained in the furnace during preparation of  $Cu_xBi_2Se_3$  single crystals. As synthesized cleaved crystals of (a)  $Bi_2Se_3$  and (b)  $Cu_{0.1}Bi_2Se_3$ .

In the second step, the quartz tube is opened and stoichiometric quantity of Bi and the remaining Se were added, pelletized and sealed in an evacuated quartz tube. Single crystals of  $Cu_xBi_2Se_3$  were grown by melting at 950°C overnight, where the growth of the crystals took place via slow cooling from 950°C to 650°C at 10°C/h and subsequent quenching in ice-water. The resultant crystals were cleaved easily along the basal plane, leaving a silvery

shining mirror like surface that turns golden nearly after 24 h in the absence of the standard procedures used for preventing the materials from oxidation.

## **2.2.** Synthesis of Nanomaterials

Bismuth nitrate pentahydrate (Bi(NO<sub>3</sub>)<sub>3</sub>.5H<sub>2</sub>O) (99.99%), Sodium Sulphite (Na<sub>2</sub>SO<sub>3</sub>) (99.99%), Selenium powder (99.99%), Nickel Nitrate Hexahydrate (Ni(NO<sub>3</sub>)<sub>2</sub>, 6H<sub>2</sub>O) (99.99%) were purchased from Sigma Aldrich. Ethylenediaminetetraacetic Acid (EDTA) and Ascorbic Acid were purchased from Alfa Aesar. All chemicals used were of analytical grade and were used as received without any further purification. All of the solutions were prepared with deionized water.

In this usual synthesis process, hierarchical Bi<sub>2</sub>Se<sub>3</sub> NFs were grown using  $(Bi(NO_3)_3.5H_2O)$  and Na<sub>2</sub>SeSO<sub>3</sub> as sources of Bi<sup>3+</sup> and Se<sup>2-</sup>, respectively. In the chemical bath, bismuth chelate was prepared with the solution of 4 ml of 0.1 M Bi(NO<sub>3</sub>)<sub>3</sub>.5H<sub>2</sub>O and 80 ml of 0.1 M EDTA. 4 ml of 0.5 M Ascorbic acid, as a reducing agent, was added to the mixture under constant stirring. The pH was maintained at around 8.50 by adding aqueous ammonia solution drop by drop until the solution turns transparent. In a separate system a 0.1 M Na<sub>2</sub>SeSO<sub>3</sub> solution was prepared by mixing 0.25 M Na<sub>2</sub>SO<sub>3</sub> with 0.1 M Se powder at 80°C with constant stirring for 8 hrs. Then around 8 ml of the nascent Na<sub>2</sub>SeSO<sub>3</sub> solution was added dropwise to the bismuth solution. After vigorous stirring for 30 min, the solution was kept in a 100 ml Teflon liner, sealed in an autoclave and heated at 175°C for 24 hrs. The autoclave was furnace cooled to room temperature. The product was subject to centrifugation at 8000 rpm for 10 min. The resultant material was washed with distilled water and absolute ethanol a number of times to eliminate all of the impurities. After that the solid product was dried in an oven at 70°C for few hours. For Ni doped Bi<sub>2</sub>Se<sub>3</sub> nanostructures, 4 ml of 0.1 M Ni(NO<sub>3</sub>)<sub>2</sub>, 6H<sub>2</sub>O was added to the Bismuth chelate prior to the addition of freshly prepared Na<sub>2</sub>SeSO<sub>3</sub> solution. All the other procedures were remained as mentioned above.

## 2.3. Characterization Techniques

#### 2.3.1. X-ray Diffraction

X-ray Diffraction (XRD) is one of the primitive conventional methods for characterization and identification of crystalline solid substances because crystalline materials act as 3D diffraction gratings for X-ray wavelengths similar to the spacing of planes in a crystal lattice discovered by Max von Laue in 1912 [6]. In 1916 Debye and Scherrer first obtained the powder diffraction pattern [7]. XRD provides structural information of a material such as phase composition, lattice parameters, strain in the structure, crystal orientation as well as grain size, thermal expansion, *etc*.

**Principle:** The interatomic distances in molecules or the interplanar spacing in the crystals are comparable to the wavelength of X-rays which causes X-rays to be diffracted from a crystalline sample when it is subjected to the irradiation over it. The diffraction follows the Bragg's law:

$$2d \,\sin\theta = n\lambda \tag{2.1}$$

where, *d* is the interplanar spacing,  $\theta$  is the glancing or rather diffraction angle, *n* is the order of diffraction and  $\lambda$  is the wavelength of incident ray.

In XRD analysis, X-ray beam is incident over a sample and scattered in different directions. The intensity of the diffracted X-rays is measured as a function of the diffraction angle (2 $\theta$ ). The intensities, broadening and shape of the obtained peaks deliver data about the atomic basis, crystal perfection and particle size of the sample. The experimentally acquired diffraction pattern is unique for a sample and is compared with various standard existing data by the joint committee on powder diffraction standards (JCPDS), thus the definite composition of the sample can be realized. XRD measurements of the samples (single crystals and powder) were performed

in room temperature and pressure using X-ray diffractometer (Bruker D8 Advance, Germany). The X-ray source is Cu X-ray having a wavelength of Cu K $\alpha$  lines with a wavelength of 1.5406 Å. The filtered Cu K $\alpha$  radiation was used for recording the diffraction pattern where the value of 2 $\theta$  was varied from 10° to 80°. Fullprof software was used for X-ray profile analysis, further to determine structural parameters.



**Figure 2.2** Scheme of different components of an XRD. The circle represents the goniometer where the sample is placed in the centre. A divergent source of X-rays is focused on the flat plate sample which then diffracted and collected by the detector. The diffraction pattern is recorded by rotating both the source and the detector at an angle  $\theta$ , keeping the sample fixed.



**Figure 2.3.** Schematic of the x-ray photoelectron spectroscopy showing its basic components.

#### 2.3.2. X-ray Photo Electron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is a broadly used spectroscopic technique which qualitatively as well as quantitatively detects the elemental identification and electronic states of elements present in a sample, relative composition of the constituents in the surface region and the valence band structure of the materials. It was established by the noble laureate Swedish physicist Kai Siegbahn in 1964 [8].

**Principle:** XPS implicates the photo-ionization and investigation of the kinetic energy distribution of the emitted core level electrons. Here the sample is illuminated with soft X-rays of sufficient energy of 100 to 2500 eV, resulting in the excitation of bound state electrons which leads to the ionization and emission of core electrons depicted in Figure 2.3. The ejected photoelectrons' kinetic energies are measured with a hemispherical electron analyzer which produces a binding energy spectrum of the photoelectrons based on the concept of the photoelectric effect according to the relation coined by Ernest Rutherford [9]:

$$E_B = h\nu - (E_k + \phi) \tag{2.2}$$

Where the kinetic energy of the emitted photoelectrons is termed as  $E_{k}$ , the photon energy is designated as hv, the work function of the spectrometer is  $\Phi$  and  $E_B$  is the binding energy of the photoelectrons. All samples of the present work were analyzed using an X-ray photoelectron spectrometer (XPS) (VG Multilab 2000-Thermo Scientific, USA, KAlpha) with a multichannel detector, which can endure high photonic energies from 0.1 to 3 keV. The pressure inside the ion-pumped analysis reactor is sustained at 1.0  $\times 10^{-9}$  mbar throughout the data procurement. The shifting in the binding energy values as a result of surface charging effects is rectified using the C1s peak with a binding energy value of 285 eV taken as the standard reference. The accuracy of the binding energy values is within  $\pm 0.2$  eV.

#### 2.3.3. Raman Spectroscopy

Raman spectroscopy is a spectroscopic procedure used to observe the vibrational, rotational and other low-frequency modes of molecules. It is based on the Raman Effect, discovered by Indian physicist C. V. Raman in 1928 [10, 11]. Raman Effect is the phenomenon where there is a change of wavelength of a monochromatic beam of light when scattered from a medium.

**Principle:** Raman is a light scattering technique, whereby a molecule scatters incident light from a high intensity laser light source. Most of the scattered light is at the same wavelength as the laser source and does not provide useful information – this is called Rayleigh Scatter. However, a small amount of light (typically 0.0000001%) is scattered at different wavelengths which depend on the chemical structure of the analyte – this is called Raman Scatter. Raman Effect arises when electric field vector of the incident photon interacts with electric dipole of the molecule. Raman spectroscopy is a form of vibrational spectroscopy. In quantum mechanical terms, the scattering can be regarded as exciting the system to a 'virtual' state. The system exchanges energy with the incident photon and subsequently decays to a vibrational energy level above or below that of the initial state. In other words, incident and scattered photons exhibit a frequency shift corresponding to the energy difference which is termed as Raman shift. The scattered photon frequency either up- or down-shifted relative to that of the incident photon. The downshifted and upshifted components are termed as Stokes and Anti-Stokes lines, respectively (Figure 2.4). Raman spectrum is a plot of the detected number of photons versus Raman shift from the incident laser frequency.



**Figure 2.4.** Raman transitional scheme (a) An electron is excited from ground state and falls back to the original position (b) An electron is excited from the ground state and falls to a vibrational level (c) An electron is excited from a vibrational level and falls to the ground level.

Classically, the interaction of light with the molecule can be pictured as the perturbation of the molecule's electric field. This interaction induces a dipole moment which is proportional to electric field strength and the molecular polarizability  $\alpha$ . A molecular vibration is Raman active only if there is a modulation of the molecular polarizability by the vibration [12].

$$\left(\frac{\partial \alpha}{\partial Q}\right) \neq 0 \tag{2.3}$$

Where  $\alpha$  is the molecular polarizability which is a measure how an electron cloud around a molecule can be distorted, Q stands for the normal coordinate of vibration. Similar to FTIR, Raman spectroscopy is a form of vibrational spectroscopy. Unlike IR spectroscopy, the interaction of radiation with matter is quite different in Raman spectroscopy. The IR-band arises due to change in the dipole moment of the molecule upon interaction with the incident radiation. The interaction is possible only when radiation field electric vector oscillates at the same frequency as the dipole moment. For IR active mode, the net change in permanent dipole moment must be modulated by normal vibration.

$$\left(\frac{\partial\mu}{\partial Q}\right) \neq 0 \tag{2.4}$$

Where  $\mu$  is the dipole moment of the molecule.

Some of the Raman active modes are forbidden in IR, and other vibrations may be observed by both the techniques at significantly different intensities; therefore, Raman and IR spectroscopy gives a complementary image of molecular vibration. In 1928, the first-ever Raman 'instrument' was constructed which used monochromatized sunlight as a light source and human eye as a detector. The modern instrument typically consists of a laser, notch filter, a few lenses, and detector. The laser is used as a light source due to its high monochromaticity and high beam fluxes. When monochromatic light is irradiated on a sample, the inelastically scattered light contains a spectrum of a wavelength longer and shorter than the excitation wavelength, which corresponds to the molecular vibration modes or crystal phonons. These bands are specific to molecular vibrations since the sample contains different materials having different vibrational modes. Raman Effect is very week process (typically Stokes lines are ~ 105 times weaker than the Rayleigh scattered components). Therefore, intense light sources and low noise detectors are used [13]. To remove elastically scattered a portion of the light from the sample, Raman spectrometer uses notch filter which allows only the Raman scattered radiation to reach the detector.

Raman spectrometer is coupled with an optical microscope which is capable of giving conventional images along with Raman spectra from a particular spot on the sample. The microscope is capable of focusing the laser beam to a small spot (~ 1 micron) on the sample. Scattered light from the sample again passes back through the microscope optics into the spectrometer, detected by Charge Coupled Detectors (CCD) and a computer is used for data acquisition and curve fitting. CCD detectors are employed due to their low dark current, high quantum efficiency, and multichannel capability. Raman scattering measurements of the samples are carried out using a Labram-HR 800 spectrometer with excitation radiation (wavelength of 488 nm) from an argon ion laser at spectra with a resolution of 1 cm<sup>-1</sup>.

#### 2.3.4. Field Emission Scanning Electron Microscopy

A scanning electron microscope (SEM) uses a beam of electrons to image samples in a raster scan pattern. SEM is one of the most heavily used microscopic instruments in research areas today because of its extremely high magnification, larger depth of focus, higher resolution and ease of sample observation [15].

**Theory:** SEM uses a beam of electrons to image the samples. A precise selection of electron energies over a desired range makes it possible to produce an image with high resolution. An SEM consists of the following components: (i) an electron gun, (ii) electromagnetic lens system, (iii) detectors and (iv) stage or sample holder. The electron gun provides an intense beam of high energy electrons. There are two type of guns, which are Thermionic gun and Field emission gun. The thermionic gun uses a heated filament to overcome the work function of the filament material, such that the electron can escape from the material itself. While the field emission gun uses a large electrical potential gradient across the filament to pull out the electrons. The electron beam follows a vertical path through the column of the microscope. It passes through the electromagnetic lenses which focus and direct the beam down towards the sample.

The high energy electrons upon interaction with the samples either undergo inelastic scattering with the atomic electrons or elastic scattering with the atomic nucleus. As a result of electron sample interaction backscattered electrons (BSEs), secondary electrons (SEs), and characteristics X-rays are produced. Several detectors are employed to detect these BSE electrons, SE electrons (Everhart-Thornely detector) and X-rays. The SE produces a most detailed image of the surface of an object, while BSE image can provide atomic number contrast in addition to topographic contrast. X-ray detectors give information on the composition of a substance (Figure 2.5).

The stage holds the sample on small stainless steel screws called 'stub' (size approx.: 8 x 8 mm). The stage can be placed at different angles and can be

rotated to make different images at different orientations. A modern electron microscope uses field emission technology for ultra-high resolution  $\sim 0.5$  nm, magnification  $\sim x 1,000,000$  of electron imaging, which is far better than compared to conventional scanning electron microscopes. The combination of higher magnification, greater resolution, larger depth of field, compositional information and user-friendliness of the apparatus and general simplicity of the image interpretation makes the SEM as one of the most heavily used instruments for research purposes.



**Figure 2.5.** Schematic representation of electron-sample interaction in FESEM.

Sample preparation is relatively easy in SEM. A thin metallic film of goldpalladium about 2 nm thickness is sputter coated on the samples and viewed under the SEM. The surface morphology of ZnO films is observed by field emission scanning electron microscopy (FESEM, Supra 55 Zeiss, UK). The system is also equipped with EDS analyzer (Oxford Instruments, UK), which is used for compositional analysis ZnO films.

#### 2.3.5. Transmission Electron Microscopy

A transmission electron microscope (TEM) is a very potent tool for material characterization on the microscopic scale. A TEM provides information about the microstructural, crystal structure and micro-chemical state with a high spatial resolution from each of the microscopic phases individually [16].

**Theory:** TEM uses a high energy electron beam to 'see through' the specimen. The electron beam interaction (Figure 2.6) with the sample gives the following results:

- A part of the high energy electron beam gets transmitted, and part of it scattered while passing through the specimen.
- Transmitted electrons suffer no interaction and no loss of energy in the specimen which carries information about the structure of the sample. Elastically scattered electrons get diffracted from their original path while passing through the specimen, without loss of energy and transmitted through the remaining portion of the specimen.
- All incident electrons which are scattered by some atomic spacing will be scattered by the same angle and will follow the Bragg's law. This diffracted beam carries the information about the orientation, atomic arrangements, and phases present in the area being examined.
- The transmitted beam gives a bright field image of the specimen. A dark field image is formed when one of the diffracted beams is selected for imaging.
- The incident electrons also inelastically interact with the specimen, then lose their energy due to this interaction and transmitted through the rest of the specimen. The loss of energy due to the inelastic scattering of electrons (Electron Energy Loss Spectroscopy (EELS)) can be measured. This information can be used to determine

elemental composition, chemical bonding and valence and conduction band electronic properties.

Similar to SEM, a modern TEM is composed of filament, an objective lens system, magnification system, a specimen stage and data recording and chemical analysis system. Sample preparation in a TEM is essential because the sample has to be thin enough to pass the electron beam through it. JEOL JEM-2100 and JEOL 3010 with UHR pole piece which is a computercontrolled high-resolution transmission electron microscope (HRTEM) are used to characterize the samples in our research work. The samples are prepared by sonicating the glass substrate with as-grown Bi<sub>2</sub>Se<sub>3</sub> present on the surface. The sonication process is carried out for 30 minutes in propanol. It results scrapping away of the Bi<sub>2</sub>Se<sub>3</sub> nanostructures from the substrate and dispersion in the propanol. This solution is cast on to copper TEM grid using a micropipette and allowed to dry for another 30-60 minutes inside a heating furnace, such that only Bi<sub>2</sub>Se<sub>3</sub> samples are left behind. The Bi<sub>2</sub>Se<sub>3</sub> samples are examined using TEM in the bright field as well as dark field imaging modes. Modern high-resolution transmission electron microscopy (HRTEM) is the ultimate tool for imaging at the atomic scale and has excellent analytical performance. HRTEM images are analyzed using ImageJ software, which is a public domain Java-based image processing program developed at the National Institutes of Health, USA.

#### 2.3.6. Field Electron Emission

The theory of electron emission from metals under the influence of strong electric fields has been applied in field electron and ion microscopy. Adsorption and desorption from surfaces, metal, and semiconductor interface studies have been performed by Gomer, Dyke and Dolan, Swanson and Bell and Gadzuk and Plummer [17]. Although field emission was first observed by R.W. Wood in 1897, theoretical predictions of the current voltage characteristics were not particularly successful, since field emission was viewed as a classical process in which electrons were

thermally activated and traversed a field reduced potential barrier. A satisfactory theoretical explanation of field emission had to wait for the advent of quantum mechanics. Using Schrödinger's wave theory, Fowler and Nordheim satisfactorily explained field emission as the quantum mechanical tunneling of electrons from the metal into vacuum under the influence of the applied electric field. The now commonly referred to Fowler-Nordheim (F-N) equation, describes the relation between the emission current density J, the surface work function, and the applied electric field strength F.



**Figure 2.6.** Schematic representation of TEM imaging system (*a*) Diffraction Mode (SAED) (*b*) Imaging Mode



Figure 2.7. A typical laboratory field electron emission setup

**Theory:** For field emission the electrons need to escape from a metal surface. For this they need to have sufficient energy to overcome the potential barrier across the metal-vacuum interface. This quantity is called the work function and corresponds to the potential difference between the Fermi level (EF) of the metal and the field free vacuum (Ev). The work function is a surface property of the material and depends on the electronic structure and orientation of the crystal plane. It differs for different crystallographic orientations of 4.36 eV for the (112) face to 4.95 eV for the (110) crystallographic orientation. The work function plays a dominant role in determining electron emission characteristics of metals.

Field emission investigations were carried out in a planar diode configuration in all-metal ultrahigh vacuum (UHV) chambers, which were evacuated to a base pressure of  $\sim 1 \times 10^{-8}$  mbar. A typical diode configuration consisted of a phosphor-coated semi-transparent indium tin oxide glass disc (a circular disc having a diameter of  $\sim 50$  mm), which acted as an anode. A Ni doped Bi<sub>2</sub>Se<sub>3</sub> nanostructure sprinkled onto a piece of UHV-compatible conducting carbon tape pasted on a copper rod holder (diameter  $\sim 5$  mm) served as the cathode. The emission current was

measured by a Keithley electrometer (6514) by sweeping a DC voltage applied to the cathode in steps of 40 V (0–40 kV, Spellman, U.S.). The stability of the field emission current was investigated using a computercontrolled data acquisition system with a sampling interval of 10 seconds. Special care was taken to avoid any leakage current using shielded cables and proper grounding. Field emission images were recorded using a digital camera (Canon SX150 IS).

# 2.3.7. Superconducting Quantum Interference Device (SQUID)

Superconducting Quantum Interference Device (SQUID) is one of the most effective and sensitive ways of measuring magnetic properties. The SQUID consists of two superconductors separated by the thin insulating layers to form two parallel Josephson junctions. The SQUID magnetometer can detect the incredibly small magnetic field. In SQUID magnetometer, the magnetizing field is provided by a superconducting electromagnet [18]. The sample is surrounded by a superconducting sensing coil, which is coupled through superconducting circuitry to a SQUID device.

The magnetic moment of the sample causes a change of flux in the sensing coil, introducing a supercurrent. This supercurrent will then change the flux through the SQUID, and it results in a change of SQUID output signal which is then picked up by the gradiometer [19]. The routine measurements in SQUID magnetometers can be performed in two ways. The first measurement is the field dependence of magnetization at constant temperature M -H, and the second is the temperature dependence of the magnetic materials under constant magnetic field M- T. According to the cooling process, temperature dependent measurements can be further performed by zero-field cool (ZFC) and field cool (FC) modes, respectively. In zero-field cooling measurements, the magnetic sample is cooled from room temperature to low temperature without applying the magnetic field. On the other hand, in field cooling measurements, the sample is cooled from

room temperature to low temperature in the presence of an applied magnetic field.



Figure 2.8. Schematic diagram of SQUID

In the present work, the magnetic measurements were recorded using a quantum design SVSM-050 super conducting quantum interference device (SQUID). The temperature ranges were from 5 K to 400 K for temperature dependent magnetic studies, and the magnetic field varies from -7 Tesla to 7 Tesla in the field dependent measurements.

## 2.3.8. Humidity Sensing Mechanism

Humidity sensing is a process that detects the presence of humidity in the environments. Generally, humidity sensors are used for detecting humidity level in several fields of technology and our daily life such as food processing unit, public transport, health care, agriculture, device fabrication unit and in chemicals laboratories [20]. A humidity detector provides the humidity level signal to operators in the humid sensitive areas, *i.e.*, industries, pharmaceutical processing, and in the fabrication of biological products [20]. A schematic diagram of the experimental setup used for humidity sensing measurement is depicted in Figure 2.10. The devices were dried in a furnace at 50°C for 30 minutes and then used for further sensing

experiments. The saturated aqueous solutions in a closed vessel at a stable temperature can provide stable and controllable RH levels in their equilibrium states. The experiment was performed at room temperature. The saturated solutions of KOH, MgCl<sub>2</sub>.6H<sub>2</sub>O, K<sub>2</sub>CO<sub>3</sub>, Mg(NO<sub>3</sub>)<sub>2</sub>, NaNO<sub>3</sub>, NaCl, KCl and K<sub>2</sub>SO<sub>4</sub> in closed conical flasks were used to obtain ~ 8%, 33%, 43%, 52%, 63%, 75%, 86% and 97% RH levels, respectively.



Figure 2.9. Schematic diagram of humidity sensing Setup.

The electrical resistance of the present film sensor was measured in DC mode using a Keithley 2400 source meter, which was connected with computer. The humidity sensing properties were investigated by exposing Bi<sub>2</sub>Se<sub>3</sub> film sensor to various RH levels, which were achieved by several saturated aqueous solutions.

In summary, the Bi<sub>2</sub>Se<sub>3</sub> pristine and doped materials growth techniques and characterization are discussed. The magnetic measurement, field electron measurement system and humidity measurement are also discussed.

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# **Chapter 3**

# Electrical and magnetic properties of copper intercalated Bi<sub>2</sub>Se<sub>3</sub> single crystal

Bi<sub>2</sub>Se<sub>3</sub> is a 3D TI which does not show superconductivity in its pure form but can be transformed to a superconductor at low temperature when certain elements are incorporated in its crystal structure. In this chapter, the growth, structural characterization, electrical transport and magnetic properties of Cu intercalated Bi<sub>2</sub>Se<sub>3</sub> single crystals of excellent quality synthesized through an efficient two step melt growth method are described which achieve superconductivity below 4K. The superconducting state as well as the normal state is analysed meticulously, indicating the presence of a spin triplet vortex state with odd parity in the previous one and existence of antiferromagnetic correlations in the sample in the next one.

# **3.1.** Background of the Work

In the last decade, topological insulator (TI), a novel quantum state of matter, was discovered with protected edge and surface states which gets originated from their unique bulk band topology [1, 2]. Over the years, the TIs have emerged as an ideal platform for quantum computation, spintronic devices, and other applications [3-9]. They are predicted to have spinmomentum-locked metallic surface states protected by time reversal symmetry which is distinguished from an insulating bulk state [2, 3]. Their band structure topology and the spin-momentum locking mechanism are predicted to prevent any localization of the surface metallic states [4, 6]. Theoretical studies as well as experimental results [1, 5, 10-15] have shown that Bi<sub>2</sub>Se<sub>3</sub> has a large band gap of 0.3 eV, and only a single Dirac cone is present at the surface of the momentum zero point in k space associated with the surface state which is topologically protected due to time-reversal symmetry. Various reports have the confirmation that there are topological surface states present in this material [7, 8, 16-21]. It was discovered that intercalating Cu with a concentration of 0.1 to 0.6 can induce superconductivity in the 3D TI  $Bi_2Se_3$  [8, 9] with a  $T_c$  value of 3.8 K [22-28]. The sign of low temperature superconductivity found by Hor *et al.* [22] created a lot of interest in experimental and theoretical science. An induced superconductivity was achieved by Bay et al. [29] by applying high pressure on the single crystals of  $Cu_x Bi_2 Se_3$ . These results strongly indicate the existence of the Cooper pairs in the topological surface state protected with time reversal symmetry in the superconducting state of  $Cu_xBi_2Se_3$ . Thus there is a concern regarding the nature of superconductivity and the relation between the two separate states of the material: the TI and the superconductor. The origin of superconductivity in the TIs seems to be related to the existence of Andreev reflection bound gapless surface states alongside a completely gapped bulk state [23]. Recently, point contact spectroscopy measurements [28-31] in  $Cu_x Bi_2 Se_3$  superconductors

exhibited a zero bias conductance peak which indicates the existence of Majorana states. Such states emerge because of the conceivable matching symmetry bound over the grain limit of the sample due to the conjunction of TI and superconductivity. On the other hand, there is an experimental evidence of *s*-wave pairing symmetry from scanning tunnelling microscopy (STM) in superconducting  $Cu_xBi_2Se_3$  [32]. Although superconductivity was observed in  $Cu_xBi_2Se_3$  from the variation of resistance and magnetization with temperature by Hor *et al.* [22] and the nature of the spin structure in the vortex state was studied and the triplet state was discovered by Das *et al.* [24], there are actually very few studies in the literature on the electrical and magnetic properties of  $Cu_xBi_2Se_3$ .

In this chapter, we report a two-step synthesis process of single-crystalline Cu intercalated  $Bi_2Se_3$ , along with the investigation of its electrical transport and magnetic properties. These measurements show that superconductivity is induced in Cu<sub>0.1</sub>Bi<sub>2</sub>Se<sub>3</sub> at low temperatures due to the intercalation of Cu between the Bi<sub>2</sub>Se<sub>3</sub> layers. The results indicate that Cu<sub>0.1</sub>Bi<sub>2</sub>Se<sub>3</sub> is a Pauli limited superconductor, and moreover, antiferromagnetic correlations may be present in the sample in the normal state.

# **3.2.** Single Crystal Synthesis and Superconducting Property Measurement Procedures

For single crystal synthesis we have used modified two step melt growth method which has been already discussed previously in chapter 2. To investigate the superconducting property of our sample, the electrical resistance and magnetization measurements were performed down to 2 K. The standard four-probe technique, employing silver paste contacts cured at room temperature, was used for the electrical resistance measurements, with the current applied along the basal plane of the crystals. A

superconducting quantum interference device-based vibrating sample magnetometer (MPMS3 SQUID-VSM, Quantum Design) was used to measure the magnetization as a function of temperature and magnetic field. The magnetization was measured in the zero-field-cooled (ZFC) warming and field-cooled-cooling (FCC) conventions. In the ZFC convention, the sample was first cooled down to 2 K in the absence of external magnetic field. The external magnetic field was applied at 2 K and the temperature was slowly increased to 15 K along with the simultaneous measurement of the magnetization. After reaching 15 K, the magnetization was measured in the same applied magnetic field while cooling down to 2 K. This latter measurement protocol is called FCC. For all the magnetization measurements, the curves reported here have been obtained after background subtraction. This was done after doing measurements with and without samples in identical conditions of temperature and magnetic field. There are two ways the magnetic field was applied on the sample: a) "H ab" when the applied magnetic field was parallel to the plane of the sample and b)  $H \parallel c$ when the applied magnetic field was perpendicular to the plane of the sample i.e. parallel to the basal plane direction of "c".

## **3.3.** Results and Discussions

#### **3.3.1. Structural and Morphological Analysis**

Figure 3.1 (a) shows the trigonal crystal structure of Bi<sub>2</sub>Se<sub>3</sub> with R-3m space group. The values of the lattice parameters are  $a = b = 4.141\pm0.003$  Å and  $c = 28.632\pm0.005$  Å with  $\alpha = \beta = 90^{\circ}$  and  $\gamma = 120^{\circ}$  with a unit cell volume of 425.67 Å<sup>3</sup>. The backbone of the material is a five-atomic-layer long quintuple layer, which is a Se2-Bi-Se1-Bi-Se2 sequential arrangement of length 7.15 Å. The coupling inside the quintuple layer is strong, while being considerably weaker in between two quintuple layers because of the van der Waals gap of 2.43 Å. Cu can be incorporated into the Bi<sub>2</sub>Se<sub>3</sub> crystal structure either (i) by intercalation, where the Cu atoms occupy the
octahedral 3b (0, 0, 12) sites in the van der Waals gap thus increasing the c axis lattice parameter and forming a layer which induces superconductivity in Bi<sub>2</sub>Se<sub>3</sub>, or (ii) by doping, where the Cu atoms sit onto the Bi sites thus decreasing the c-axis lattice parameter due to the smaller size of the Cu atom as compared to that of the Bi atom, with no sign of superconductivity.



**Fig. 3.1.** (a) Crystal structure of  $Bi_2Se_3$  (b) XRD pattern of a single crystal of  $Cu_{0.1}Bi_2Se_3$  and (c) Powder XRD pattern of  $Cu_xBi_2Se_3$  (x=0, 0.1) with Rietveld Refinement.

Figure 3.1 (b) displays the XRD pattern of a  $Cu_{0.1}Bi_2Se_3$  single crystal. The observed peaks are indexed for (0 0 3 *n*) reflections of  $Bi_2Se_3$  of *R*-3*m* space group, with no impurity peaks visible. This outcome matches with the available reports where the atomic ratio of Cu is less than 0.3 [22, 25]. The growth of our single crystal sample is unidirectional along the standard bismuth chalcogenides crystal growth direction, which is along the *c*-axis and is confirmed by the existence of only (0 0 3*n*) reflections. The single crystals are of decent phase purity which is confirmed by high intensity peak to noise ratio, and the excellent crystalline quality is indicated by the sharp

reflections observed in Fig. 3.1 (b). The powder XRD patterns for the samples of  $Cu_xBi_2Se_3$  (x=0, 0.1) are presented in Fig. 3.1 (c). The solid (black) curves through the data are obtained through Rietveld refinement. The lattice parameters, atomic positions and occupancy of the corresponding atoms acquired from the refinements are depicted in table 3.1. From table 3.1 it is evident that the *c*-axis lattice parameter has been increased from  $c = 28.662(\pm 0.004)$  Å for Bi<sub>2</sub>Se<sub>3</sub> to  $c = 28.703(\pm 0.002)$  Å for Cu<sub>0.1</sub>Bi<sub>2</sub>Se<sub>3</sub>. As the *c*-axis is the layer-stacking direction, the increment guarantees the Cu intercalation between two neighboring quintuple layers, which is consistent with the previous report on Cu intercalated Bi<sub>2</sub>Se<sub>3</sub> samples [37] and related layered selenides [38].

**TABLE 3.1.** Structural parameters obtained from the Rietveld refinement of powder XRD.

Sample	Atom	X	Y	Z	Occupancy
Cu <sub>0.1</sub> Bi <sub>2</sub> Se <sub>3</sub>	Bi	0	0	0.40176	0.08853
<i>a=b=</i> 4.141(±0.003)Å	Se1	0	0	0	0.04095
$c = 28.703(\pm 0.002)$ Å	Se2	0	0	0.20124	0.09737
Bi <sub>2</sub> Se <sub>3</sub>	Bi	0	0	0.40276	0.09211
<i>a=b=</i> 4.142(±0.003)Å	Se1	0	0	0	0.08892
$c = 28.662(\pm 0.004)$ Å	Se2	0	0	0.20841	0.18040

Figure 3.2 (a) shows an image of the as grown ingot crystal which is silvery and shiny due to high purity and crystalline nature. For sample characterizations and measurements of various properties small pieces of crystals are cleaved shown in Fig. 3.2 (c) and (d). Figure 3.2 (b) depicts a clear FESEM image of a cleaved  $Cu_{0.1}Bi_2Se_3$  sample presenting layer by layer growths as the edges of separate layers are clearly visible.

## 3.3.2. Raman Analysis

Raman spectroscopy measurements were done over small films exfoliated from the single crystals by scotch tape. Figure 3.3 shows the Raman spectra of Bi<sub>2</sub>Se<sub>3</sub> and Cu<sub>0.1</sub>Bi<sub>2</sub>Se<sub>3</sub>. Four clear distinctive peaks are present having frequency: ~75 cm<sup>-1</sup>, ~105 cm<sup>-1</sup>, ~133 cm<sup>-1</sup> and ~175 cm<sup>-1</sup>. As the observed peaks are well matched with the previously reported experimental and calculated phonon vibration modes of Bi<sub>2</sub>Se<sub>3</sub> [39], they are assigned as follows: 133 cm<sup>-1</sup> as the  $E^2_g$  mode, 75 cm<sup>-1</sup> and 175 cm<sup>-1</sup> as the first and the second order  $A_{1g}$  modes, respectively, and 105 cm<sup>-1</sup> as the  $E^1_u$  mode. The subscript "g" denotes Raman active while "u" denotes the IR-active modes.



**Fig. 3.2 (a)** Image of an as grown single crystal of Cu<sub>0.1</sub>Bi<sub>2</sub>Se<sub>3</sub> (b) FESEM image of a cleaved single crystal (c) and (d) Images of cleaved single crystals.



**Fig. 3.3** Raman Spectra of  $Cu_x Bi_2 Se_3$  (x=0, 0.1). The inset shows significant change in the shift of  $A^2_{1g}$  peak.

With Cu-intercalation, a redshift is observed for the  $A^2_{1g}$  vibrational peak designated as the out of plane vibrations of Bi and Se2 atoms (outer Se atoms of a quintuple layer) along the *c* direction. The Cu atoms attract the Se2 atoms away from Bi atoms, as a result the Bi atoms need to spend a smaller amount of energy which relate to lower energy Raman peaks also observed previously in Cu intercalated Bi<sub>2</sub>Se<sub>3</sub> samples [37]. Because of the quantum size effects, an IR active mode is witnessed in both samples [40].

## **3.3.3. Superconducting Properties**

#### **3.3.3.1.** Analysis from Resistance Measurements

The temperature dependence of electrical resistance (R) of the Cu<sub>0.1</sub>Bi<sub>2</sub>Se<sub>3</sub> crystal is shown in Fig. 3.4. The sample shows a metallic behaviour in the normal state and the superconducting transition ( $T_{c-onset}$ ) occurs at 3.0 K (inset in Fig. 3.4). The resistance, however, does not go to zero down to the lowest achievable temperature of 1.4 K for the present experimental set-up, indicating that the normal to superconducting phase transition is not complete at this temperature. The possible reason behind the resistance not going to zero is due to a lack of a continuous superconducting path in the sample where there is a high density of weak-links and regions of low critical current. The temperature dependence of electrical resistance in the normal state of the Cu<sub>0.1</sub>Bi<sub>2</sub>Se<sub>3</sub> crystal can be fitted by two different functions above and below 65 K, as shown in Fig. 3.4. While R varies nearly linearly with temperature above 65 K, which is commensurate with the electron-phonon scattering effects in a metal, the resistance can be well fitted using the formula  $R = R_0 + AT^2$  below 65 K. This quadratic temperature dependence of resistance, when observed at a very low temperatures (~ 1-2 K or below), is suggestive of electron-electron correlations observed in a Fermi liquid ground state [41]. However, at higher temperatures, this  $T^2$  behaviour might indicate the presence of magnetic correlations including spin fluctuations [41].



**Fig. 3.4.** The temperature dependence of electrical resistance of  $Cu_{0.1}Bi_2Se_3$ in zero field showing a  $T^2$  behaviour in the normal state below 65 K. The upper inset shows the  $T_c$  onset at 3.0 K (in zero field). The lower inset shows the magnetoresistance of the  $Cu_{0.1}Bi_2Se_3$  crystal in the normal state.



**Fig. 3.5 (a)** Temperature dependence of upper critical field ( $H_{c2}$ ), for  $H \parallel ab$ , for Cu<sub>0.1</sub>Bi<sub>2</sub>Se<sub>3</sub> single crystal. The upper inset shows the low temperature (1 K to 3.5 K) resistance in different external magnetic fields H = 0, 1, 2, 4, 6, 8 and 10 kOe ( $H \parallel ab$ ). The lower inset shows the variation of activation energy as a function of the external magnetic field ( $H \parallel ab$ ) and (**b**) Comparison of the temperature dependence of  $H_{c2}$  for superconducting

Cu<sub>0.1</sub>Bi<sub>2</sub>Se<sub>3</sub> in the H || ab and H || c geometries. The inset shows the low temperature (1 to 3.8 K) resistance in different magnetic fields (H = 0, 1, 2.5, 5, 7.5 and 10 kOe) for H || c.

It may be noted in this context that the present  $Cu_{0.1}Bi_2Se_3$  single crystal sample shows a small but clear positive magnetoresistance ( $MR = \frac{R(H) - R(0)}{R(0)} X 100$ ) in the normal state (see the lower inset in Fig. 3.4) even in low fields, and this MR is found to increase with increasing applied magnetic field (MR measurements above 10 K were not performed for conserving the resources). While a paramagnetic metal is expected to exhibit a positive MR in high magnetic fields due to the orbital motion of the conduction electrons, as prescribed by the Kohler rule, a positive MR in relatively low fields may indicate the presence of antiferromagnetic correlations (see [42-44] and the references therein). The  $T^2$  dependence of electrical resistance observed below 65 K may be related to the presence of antiferromagnetic correlations in the  $Cu_{0.1}Bi_2Se_3$  single crystal sample in the normal state, which may be in the form of antiferromagnetic spin fluctuations as well.

With the application of external magnetic field, the superconducting transition shifts to lower temperature. This is shown in the upper inset of Fig. 3.5 (a) where the  $T_{c-\text{onset}}$  decreases from 3.01 K to 2.03 K when the magnetic field ( $H \parallel ab$ ) is increased from 0 to 10 kOe. The main panel of the Fig. 3.5 shows the temperature dependence of upper critical field ( $H_{c2}$ ) obtained from the onset of the superconducting transition. The points represent the different values of  $T_{c-\text{onset}}$  obtained experimentally with different values of the external magnetic field ( $H_{c2}$ ). The  $H_{c2}(0)$  value (at 0 K) was found by fitting the equation  $H_{c2}(T) = H_{c2}(0) [(1 - t^2) / (1 + t^2)]$ , where  $t = T/T_c$ , to the experimentally obtained  $H_{c2}(T)$ . The fitted equation has been previously used in intercalated Bi<sub>2</sub>Se<sub>3</sub> superconducting samples [45]. In this manner  $H_{c2}(0)$  was found to be 27.1 kOe for  $H \parallel ab$ . In the lower inset we plot the field dependence of the activation energy  $U_0$ ,

obtained using the Arrhenius plots ( $\ln R$  versus 1/T plots; R was used in the place of resistivity in this case because of the irregular shape of the sample) in different applied magnetic fields  $(H \parallel ab)$  [46]. The curve is fitted using the equation,  $U_0(H) = aH^{\gamma} \left(1 - \frac{H}{H^*}\right)^{\delta}$  [47] where *H* is the applied magnetic field,  $H^*$  is the irreversibility field, and a,  $\gamma$ ,  $\delta$  are the scaling parameters. The component  $\left(1 - \frac{H}{H^*}\right)^{\delta}$  quantifies the suppression of superconductivity because of the external magnetic field, and the variation due to decreasing critical current density is represented by the component  $H^{\gamma}$ . The equation fits well for our Cu<sub>0.1</sub>Bi<sub>2</sub>Se<sub>3</sub> sample with the irreversibility field  $H^* = 12.5$ kOe and the fitting parameters  $\gamma = -0.16$  and  $\delta = 0.96$ . A distinct parabolic behaviour is observed in the  $U_0$  versus H curve, which is ascribed to strong grain boundary pinning. In the case of the intermetallic superconductors, the dominant flux pinning is generally the inter-grain pinning because the average grain boundary spread is wider than the inter-vortex distance in these materials. Figure 3.5 (b) shows a comparison between the temperature dependence of  $H_{c2}$  for superconducting Cu<sub>0.1</sub>Bi<sub>2</sub>Se<sub>3</sub> in the  $H \parallel ab$  and  $H \parallel c$ geometries. The insets to the Fig. 3.5 (a) and (b) and the comparison depicted in Fig. 3.5 (b) show that a larger suppression of the superconducting transition temperature occurs with the application of an external magnetic field for the  $H \parallel c$  axis as compared to that for the  $H \parallel ab$ plane. By the extrapolation of the experimental  $H_{c2}(T)$  curve with the help of the equation  $H_{c2}(T) = H_{c2}(0) [(1 - t^2) / (1 + t^2)], H_{c2}(0) || ab = 27.1$  kOe and  $H_{c2}(0) \| c = 23.0$  kOe values were obtained. Thus, the electrical transport is highly anisotropic in nature in the layered Cu<sub>x</sub>Bi<sub>2</sub>Se<sub>3</sub> superconductors, as has also been observed previously [22]. Moreover, the Pauli limited upper critical field is given by  $H_P(0) = 1.84 T_c = 55.2$  kOe. In the Werthamer Helfand Hohenberg (WHH) theory [48], the orbital upper critical field of a superconductor of type-II is described by  $H_{c2} = -0.72 T_{c}$  $(dH_{c2}/dT)_{Tc}$ . This is estimated to be 19.5 kOe for  $H \parallel ab$  and 16.5 kOe for  $H \| c$ . Since  $H_{c2}^{\text{orb}}(0) < H_{c2}(0) < H_P(0)$ ,  $Cu_{0.1}Bi_2Se_3$  is thus found to be a

Pauli limited superconductor. Following table is shown comparing the value of the upper critical field of our sample with some previously reported Bi<sub>2</sub>Se<sub>3</sub> based superconductors.

Material	Value of $H_{c2}(0)$	Reference
Cu <sub>0.12</sub> Bi <sub>2</sub> Se <sub>3</sub>	1.7 T ( $H \parallel c$ ) 4.6 T ( $H \parallel ab$ )	[22]
$Sr_{0.1}Bi_2Se_3$	1.4 T ( $H \parallel c$ ) 2.1 T ( $H \parallel ab$ )	[45]
Nb <sub>0.25</sub> Bi <sub>2</sub> Se <sub>3</sub>	1.8 T ( <i>H</i> c)	[49]
Cu <sub>0.1</sub> Bi <sub>2</sub> Se <sub>3</sub>	2.3 T ( $H \parallel c$ ) 2.7 T ( $H \parallel ab$ )	This Work

**Table 3.2.** Comparison of the Upper Critical Field  $H_{c2}(0)$  of  $Bi_2Se_3$  based superconductors.

For the present sample, the Maki parameter [50] is estimated as  $\alpha = \sqrt{2}$  $H_{c2}^{\text{orb}}(0)/H_{\text{P}}(0) = 0.499$ , which is less than 1. The electronic anisotropy parameter  $\Gamma = H_{c2,ab} / H_{c2,c} = \lambda_c / \lambda_{ab}$  is about 1.2, and using the anisotropic Ginzburg-Landau (GL) formulas [51]  $H_{c2,ab} = \Phi_0/(2\pi\xi_{ab}\xi_c)$  and  $H_{c2,c} = \Phi_0/(2\pi\xi_{ab}^2)$ , with  $\Phi_0 = 2.07 \times 10^{-7}$  G cm<sup>2</sup>, the GL coherence lengths are estimated as  $\xi_{ab} = 11.9 \pm 0.1$  nm and  $\xi_c = 10.1 \pm 0.1$  nm. The GL parameters along the two field directions are defined as  $\kappa_{ab} = \sqrt{(\lambda_{ab}\lambda_c/\xi_{ab}\xi_c)}$  and  $\kappa_c = \lambda_{ab}/\xi_{ab}$  [52-54]. The value of lower critical field  $H_{c1,ab}$  has been calculated from the magnetic measurements shown below. Using  $H_{c1,ab} = (\Phi_0/4\pi\lambda_{ab}\lambda_c)(\ln\kappa_{ab} + 0.5)$  [55] and the GL formula,  $H_{c2,ab}/H_{c1,ab} = 2\kappa_{ab}^2/(\ln \kappa_{ab} + 0.5)$  gives  $\kappa_{ab} = 135.4$  and  $\kappa_c = 114.9$ . Moreover, from the  $H_{c1,ab}$ formula and  $\lambda_c = \Gamma\lambda_{ab}$  we get the corresponding penetration depths  $\lambda_{ab}(0) = 1375 \pm 40$  nm and  $\lambda_c(0) = 1619 \pm 36$  nm. While the large coherence length aids to the pinning in the grain boundaries, the higher anisotropy leads to larger  $U_0$  in the low field regime. The activation energy in low fields is given by  $U_0 = \frac{\phi_0^2 \xi}{48\pi^2 \lambda^2}$  [47]. For our sample using the value  $\xi \sim 12$  nm and  $\lambda \sim$ 

1375 nm,  $U_0$  is estimated to be ~ 145 K.

#### **3.3.3.2.** Analysis from Magnetic measurements

Temperature variation of magnetization in 10 Oe field, in the zero field cooling (ZFC) and field cooling (FC) protocols, for the Cu<sub>0.1</sub>Bi<sub>2</sub>Se<sub>3</sub> single crystal is shown in Fig. 3.6 (a). The ZFC and FC magnetization curves indicate a clear low moment paramagnetic signal in the normal state, and the paramagnetic nature persists below the superconducting transition onset (close to 3 K). The diamagnetic nature is observed only below about 2.6 K. The paramagnetic normal state does not exhibit any appreciable temperature-dependence. This behaviour is not the same with the parent compound  $Bi_2Se_3$  as well as that of the previous report in  $Cu_xBi_2Se_3$  where a diamagnetic normal state has been reported [56]. The magnetization curves in the FC and ZFC modes do not follow the same route in the superconducting state, displaying the usual behaviour of flux pinned type-II superconductors. The normal to superconducting transition, indicated by a drop in the magnetization with decreasing temperature is not completed down to 2 K, and the DC susceptibility value does not attend the maximum value of -1 (not presented here for conciseness).



**Fig. 3.6** (a) Magnetization as a function of temperature in H=10 Oe in the ZFC and FC protocols and (b) the temperature dependence of the inverse of the magnetic susceptibility.



Fig. 3.7. (a) - (e) Temperature dependence of magnetization of the Cu<sub>0.1</sub>Bi<sub>2</sub>Se<sub>3</sub> single crystal in the ZFC and FC protocols in different applied magnetic fields and (f) Temperature dependence of H<sub>c2</sub> estimated from the drop in the magnetization observed at low temperatures in different fields (shown in the inset). The points in the main panel represent the experimental data and the fitted line represents the equation written in the Fig. 3 (f).

The temperature dependence of the inverse of DC magnetic susceptibility  $(1/\chi)$  for the Cu<sub>0.1</sub>Bi<sub>2</sub>Se<sub>3</sub> single crystal is shown in Fig. 3.6 (b). In spite of the width of the data (due to low signal level), it is visible that  $1/\chi$  follows a linear temperature dependence. A straight line fitted to this data intersects the temperature axis at -21 K approximately. This indicates the presence of antiferromagnetic correlations [57] in the present sample, which is in

harmony with our electrical resistance and *MR* results presented above. The temperature dependence of the normal state magnetization of the present  $Cu_{0.1}Bi_2Se_3$  single crystal also exhibits interesting thermo-magnetic behaviour as a function of the field of measurement, which is presented in Fig. 3.7. While the bifurcation between the ZFC and FC magnetization curves in the normal state is insignificant in the low fields, a clear thermomagnetic hysteresis is observed in the intermediate fields (see Fig. 3.7 (a) – (e)). The hysteresis, however disappears in still higher fields around 20 kOe. Moreover, while the magnetization is positive (paramagnetic) and nearly temperature independent in low fields, a strong curvature (with the magnetization rising with decreasing temperature) develop in the ZFC and FC magnetization curves in higher fields along with their changeover to negative (diamagnetic) magnetization values around 2 kOe.

The temperature dependence of  $H_{c2}$  estimated from the onset of the drop in the magnetization observed at low temperatures in different fields (inset) is shown in Fig. 3.7 (f). The superconducting transition shifts towards lower temperature with the increasing magnetic field. The points in Fig. 3.7 (f) represent the experimental data and the fitted line represents the equation written in the Fig. The upper critical field at zero temperature was found to be ~ 14.4 kOe from the fitted curve. This value is quite low as compared to those obtained from the measurement of electrical resistance. However, the onset  $T_c$  seems to be nearly same in the temperature dependence of magnetization measured in 10 Oe field and the electrical resistance measured in zero field. The complicated normal state temperature dependence of magnetization in the higher fields described above probably affects the determination of the onset temperature of superconductivity from the magnetization curves.

#### **3.3.3.3. Magnetic Hysteresis Analysis**

Fig. 3.8 displays the first quadrant of the isothermal magnetic field dependence (up to 200 Oe) of magnetization of  $Cu_{0.1}Bi_2Se_3$  single crystal

measured at 2 K. The lower critical field was estimated by fitting a straight line to the initial portion of the magnetization curve and locating the field where the magnetization starts to turnaround with respect to the extrapolated straight line. At 2 K the lower critical field  $H_{c1}$  of the sample of Cu<sub>0.1</sub>Bi<sub>2</sub>Se<sub>3</sub> was found to be 2 Oe [inset (a) of Fig. 3.8].



**Fig. 3.8** Isothermal field dependence of magnetization of Cu<sub>0.1</sub>Bi<sub>2</sub>Se<sub>3</sub> at 2 K. Inset (**a**) shows the expanded portion in the low field region and (**b**) shows the entire curve up to 70 kOe.

Unlike the usual type-II superconductors, the magnetization in present study sample rises very sharply with the magnetic field over a very short range just above the lower critical magnetic field  $H_{c1}$ . After this, the magnetization increases slowly with increasing magnetic field attaining a maximum value of -6.4×10<sup>-7</sup> emu at 28 Oe. Subsequently, with further increasing magnetic field, the magnetization starts decreasing and finally combines with the diamagnetic curve of the normal state in high fields [see the inset Fig. 3.8 (b) for comparison]. At 2 K, the sample shows diamagnetic behaviour in the entire field-range of measurement up to 70 kOe. The temperature dependence of magnetization for the present Cu<sub>0.1</sub>Bi<sub>2</sub>Se<sub>3</sub> single crystal presented above also indicates that the sample is diamagnetic in high fields. Similar field dependence of magnetization has been observed previously in

the  $Cu_x Bi_2 Se_3$  superconductor [24], where it has been linked with the unique odd parity spin triplet pairing mechanism favored by strong spin orbit coupling, which is a hallmark of the Bi<sub>2</sub>Se<sub>3</sub> based TIs. A magnetic field which is non-uniform in the vortex region is induced by the vortex current. The spins of the spin-triplet pairs are polarized by this magnetic field resulting in the production of a non-uniform spin magnetization in the crystal. Then, in the superconductor the total magnetic flux is not only due to the vortex current but also has a contribution from the spin magnetization. The spin magnetization considerably affects the vortex current causing current inversion in some portion of the vortices, which generates an attractive force amongst the vortices. The attractive force assists the vortices to enter into the crystal in applied magnetic fields just above  $H_{c1}$ . This accumulation of vortices due to the attractive force influences the magnetization curve causing a rapid rise of the magnetization just above  $H_{c1}$ as observed in our sample. The observed magnetization behaviour of the present sample in the vicinity of the lower critical field is therefore consistent with the concept of a superconductor with spin triplet pairing [24, 58].

For a cross-check, we have performed additional isothermal M versus H measurements on another piece of a sample prepared by the one step melt growth method (all stoichiometric precursors in powder form mixed and heated at 950°C overnight, slowly cooled to 620°C and quenched in icewater). The magnetic hysteresis due to flux line pinning in the mixed state of this superconducting sample is shown in the inset of Fig. 3.9 (a). The variation of magnetization with the applied magnetic field in this sample (see Fig. 3.9) is not very different from the previous one discussed above. In this second sample, the lower critical magnetic field is found to be 4 Oe in the same procedure as done for the previous one [see inset (b)]. This value is quite similar to that of the previously reported value [38] as well as Sr intercalated Bi<sub>2</sub>Se<sub>3</sub> superconducting sample [45]. As shown in main panel of Fig. 3.9, where the magnetic signal is presented up to 70 kOe, the

magnetic signal attains the highest value at ~16 kOe and a diamagnetic signal finally appears in much higher fields.



**Fig. 3.9** Isothermal field dependence of magnetization for a second  $Cu_{0.1}Bi_2Se_3$  sample prepared by the one step melt growth method. Inset (a) shows the expanded low field part for the envelope magnetization curves. The lower curve in this inset is for increasing field and the upper curve is for decreasing field. Inset (b) shows the virgin magnetization curve initiated from the ZFC state in low fields.

While it is known that  $Bi_2Se_3$  is diamagnetic [56] in nature, Cu and Se can form complicated compounds such as  $CuSe_2O_5$  [59, 60], which shows antiferromagnetic behaviour, and  $Cu_2Se$  [61], which shows diamagnetic and weakly paramagnetic behaviour. According to previous report on bulk  $Cu_xSe_y$  [62], they cannot be considered as simple paramagnetic materials and also the value of magnetization depends on the ratio of Cu and Se atoms. In our Cu<sub>0.1</sub>Bi<sub>2</sub>Se<sub>3</sub> single crystal it appears that the diamagnetism is related to the parent compound Bi<sub>2</sub>Se<sub>3</sub>, and the low field paramagnetism as well as the superconductivity at low temperatures is due to Cu intercalation. The indications of antiferromagnetic correlations observed in our Cu<sub>0.1</sub>Bi<sub>2</sub>Se<sub>3</sub> single crystal could be because of the formation of a small amount of  $Cu_xSe_y$  (1- 2 %). While our XRD pattern does not indicate the presence of  $Cu_xSe_y$ , 1-2 % of such impurity may possibly go un-noticed in such an experiment, due to XRD detection limit. The thermo-magnetic hysteresis between the ZFC and FC magnetization curves above the superconducting transition temperature of the present  $Cu_{0.1}Bi_2Se_3$  single crystal hints towards the presence of some kind of magnetic domains or clusters. It is possible that the small amount of  $Cu_xSe_y$  present in our sample is not distributed in a very spatially uniform manner, and this leads to the formation of magnetic domains/nano-regions. Either there are antiferromagnetic correlations within these domains/nano-regions, and/or there may be weak antiferromagnetic correlations in-between these domains.

## **3.4.** Summary

In summary, superconducting single crystals of Cu intercalated Bi<sub>2</sub>Se<sub>3</sub> were successfully synthesized through the modified two step melt growth process. The synthesis process was chosen to avoid the formation of Cu<sub>2</sub>Se, since Cu<sub>2</sub>Se is known to inhibit the intercalation of Cu atoms into the van der Waals gap between the  $Bi_2Se_3$  layers. The XRD results indicate the single crystalline nature of the sample as well as the intercalation of Cu in the layer structure of Bi<sub>2</sub>Se<sub>3</sub>, and this is also confirmed by the Raman analysis. The  $H_{c2}$  versus  $T_c$  phase diagram obtained with the help of the electrical resistance measurements indicate that in the zero temperature limit the  $H_{c2}$  can be as high as 27.1 kOe when the field is applied parallel to the *c*-axis, though the electrical transport is found to be highly anisotropic in nature. Estimation of the superconducting parameters indicate that Cu<sub>0.1</sub>Bi<sub>2</sub>Se<sub>3</sub> is a Pauli limited superconductor. The field dependence of magnetization in the superconducting state seem to be consistent with a spin triplet vortex state with odd parity. In the normal state, on the other hand, the temperature dependence of magnetic susceptibility and the sign of the magneto-resistance indicate the presence of antiferromagnetic correlations in the sample.

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## **Chapter 4**

# Effect of Cu intercalation on humidity sensing properties of Bi<sub>2</sub>Se<sub>3</sub> single crystals

In this chapter phase pure single crystals of  $Cu_xBi_2Se_3$  (x = 0, 0.13 and 0.25) has been investigated as a potential material for humidity sensors. The chemiresistive humidity sensing performance of the  $Cu_{0.25}Bi_2Se_3$  single crystals exhibit high sensitivity (~849%) with decent response and recovery time of 24s and 25s respectively, negligible hysteresis (<1%) and excellent stability within 8-97% RH range at room temperature. The effect of intercalation on humidity sensing properties is investigated using Freundlich isotherm model and Langmuir Adsorption isotherm model approving role of faster conduction of water vapour over the surface with single active site for adsorption-desorption process confirming improved sensing performance of Bi<sub>2</sub>Se<sub>3</sub>TIs with Cu intercalation.

## 4.1. Background of the Work

The topological insulator (TI) is defined as material showing insulating behaviour in the bulk but provides topologically protected conducting surface states having time reversal symmetry [1, 2]. In other words, we can define topological insulator as materials which have insulating bulk properties and surfaces containing conducting electronic states [3, 4]. Due to strong spin-orbit interaction the possibility of electron backscattering by surface defects get reduced in TIs. This lowers the surface resistivity and formation of topologically protected surface states [5, 6]. Three dimensional TIs such as Bi<sub>2</sub>Se<sub>3</sub>, Bi<sub>2</sub>Te<sub>3</sub> and Sb<sub>2</sub>Te<sub>3</sub> are referred as second generation of TIs which has great potential for device applications due to their layered structure in which the adjacent layers are bonded together with weak van der Waals forces [7-12]. Over the last decade basic research on TIs emerged as one of the leading candidate due to their significant role in development of quantum computing, spintronic devices, field emitters, etc. [13-15]. The engineering of device and its application requires detailed investigation of material properties under different practical condition. It has been reported that the effect of surrounding analytes has a major impact on transport properties of TI in terms of its sensing properties [16]. Various instrumentation like angle resolved photoelectron spectroscopy (ARPES), scanning tunnelling microscopy (STM) can be used to confirm these behaviors, whereas due to their portability and high cost, striving for opting simple and economic electrical measurement is needed to investigate the fundamental properties for device development and innovation [17]. Humidity sensors have drawn a huge attention by researchers during recent time due to their versatile applications in wide range of areas like agriculture, aerospace, electronics, chemical, food storage industries, etc. [18, 19]. Other than this it has contributed towards better indoor occupational conditions leading to a healthier and comfortable life. Basically humidity sensing is a surface phenomenon and large number of

metal oxides; [18] ferrites [20] and polymers [21] are widely investigated and used as humidity sensors. Whereas presence of both strong spin-orbit interaction and layered structure topological insulators shows an improved surface conduction which is required for improved moisture sensing performance of any sensor device. To the best of our knowledge there is no literature available for the humidity sensing application of the Bi<sub>2</sub>Se<sub>3</sub> TI, thus motivating us to open a new window in the never-ending progress of research.

In this work, we report the synthesis of  $Cu_xBi_2Se_3$  (x = 0, 0.13 and 0.25) single crystals by self-flux method. The crystal structure and intercalation of Cu in Bi\_2Se\_3 were analysed using X-ray diffraction (XRD) and Raman spectroscopic measurements. Basically we have performed two-terminal measurements for  $Cu_xBi_2Se_3$  (x = 0, 0.13 and 0.25) single crystals in different humidity surrounding to know their sensitivity towards change in ambient environment. Interestingly, theoretical evidences in the form of Freundlich and Langmuir adsorption isotherm model are in well relation with experimental results. These theoretical fitting evidences help to formulate a significant qualitative humidity sensing mechanism of Bi\_2Se\_3 topological insulators which proves its multifunctional application.

## 4.2. Synthesis Procedure

For single crystal synthesis we have used modified two step melt growth method which has been already discussed previously in chapter 2.

## **4.3.** Results and Discussion

## 4.3.1. Structural and Morphological Analysis

 $Bi_2Se_3$  boasts of a layered crystal structure with a triangular lattice within one layer. It has a trigonal crystal structure with space group of R-3m. The material consists of a series of quintuple layers along the *c*-direction where a quintuple layer is a five-atomic-layer unit arranged as the Se2-Bi-Se1-BiSe2 sequence [15]. The length of a quintuple layer is 7.15 Å. The coupling within the quintuple layer is strong but is much weaker between two quintuple layers due to the presence of van der Waals gap of 2.43 Å. Copper atoms can enter into the Bi<sub>2</sub>Se<sub>3</sub> crystal in two different ways. Firstly, by the intercalation of Cu atoms in the van der Waals gap between Bi<sub>2</sub>Se<sub>3</sub> layers which results in the increase of *c*-axis lattice parameter. This incorporation of Cu atoms, which in turn form a layer of these atoms, induces superconductivity in the material. Another way the Cu atoms can go into the crystal is to replace the Bi atoms which result in a decrement of *c*-axis lattice parameter as the atomic radius Cu atom is less than that of Bi atoms. Fig. 4.1 (a) displays the XRD pattern of single crystal of  $Cu_{0.13}Bi_2Se_3$  (inset shows the photo graph of single crystal) and Fig. 4.1 (b) displays the powder XRD pattern of  $Cu_x Bi_2 Se_3$  (x = 0, 0.13 and 0.25). No traces of impurities were observed however shift in 2 thetas were evidence due to Cu intercalation. Indexing of the observed peaks depicts only  $(0 \ 0 \ 3n)$ reflections with the hexagonal axis, R-3m space group of Bi<sub>2</sub>Se<sub>3</sub>. This result is in accordance with the available reports of a pure single crystal sample where the nominal Cu ratio is not larger than 0.15 [22]. The presence of only  $(0\,0\,3n)$  reflections confirms unidirectional crystal growth along the *c*axis, which is the standard layered crystal growth direction for Bismuth chalcogenides such as Bi<sub>2</sub>Se<sub>3</sub>, Bi<sub>2</sub>Te<sub>3</sub>, etc. The high intensity peak to noise ratio and sharp reflections observed in Fig. 4.1 (a) for the grown single crystals confirm high phase purity and excellent crystalline quality for intrinsic property measurements. Rietveld refined powder XRD patterns for the samples  $Cu_xBi_2Se_3$  are shown in Fig. 4.1. (b). The solid black curve represents the results obtained from Rietveld refinement of the data. The parameters obtained from the refinements are listed in Table 4.1. It is observed that the lattice parameter along the c- axis increases from c =28.665 $\pm$ 0.002 Å for Bi<sub>2</sub>Se<sub>3</sub> to  $c = 28.734 \pm 0.003$  Å for Cu<sub>0.25</sub>Bi<sub>2</sub>Se<sub>3</sub> while 'a' and 'b' lattice parameters remain almost same. As 'c' axis is the layer stacking direction, the increment confirms the Cu-intercalation into the two

adjacent quintuple layers, which is consistent with the previous report [23]. It can be inferred by an analogy to the behaviour in related layered selenides [24], that the intercalated Cu in the van der Waals gap partially occupies the octahedrally coordinated 3b (0, 0, 12) sites in the R-3m space group. Fig. 5.1 (*e-g*) shows the FESEM images of the edge of the single crystals of pure Bi<sub>2</sub>Se<sub>3</sub>, Cu<sub>0.13</sub>Bi<sub>2</sub>Se<sub>3</sub> and Cu<sub>0.25</sub>Bi<sub>2</sub>Se<sub>3</sub>, respectively. All the images confirm the layer by layer growth as the edges of separate layers are clearly visible.

**Table 4.1.** Structural parameters obtained from Rietveld refinement method of powder X-ray diffraction patterns shown in Fig. 4.1 (b).

Sample	Atom	X	Y	Z	Occupancy
Bi <sub>2</sub> Se <sub>3</sub>	Bi	0	0	0.40276	0.09211
<i>a=b=</i> 4.141±0.003Å	Se1	0	0	0	0.08892
<i>c</i> =28.665±0.002Å	Se2	0	0	0.20841	0.18040
Cu <sub>0.13</sub> Bi <sub>2</sub> Se <sub>3</sub>	Bi	0	0	0.40142	0.08779
<i>a=b=</i> 4.141±0.002Å	Se1	0	0	0	0.03658
<i>c</i> =28.713±0.003Å	Se2	0	0	0.20091	0.08305
Cu <sub>0.25</sub> Bi <sub>2</sub> Se <sub>3</sub>	Bi	0	0	0.40089	0.08478
<i>a=b=</i> 4.141±0.004Å	Se1	0	0	0	0.01031
<i>c</i> =28.734±0.003Å	Se2	0	0	0.20024	0.02358

## 4.3.2. Raman Analysis

Raman spectra of  $Cu_x Bi_2 Se_3$  single crystals are shown in Fig. 4.1 (c). There are only four prominent characteristic peaks which are occurred at the frequency of 75 cm<sup>-1</sup>, 105 cm<sup>-1</sup>, 133 cm<sup>-1</sup> and 175 cm<sup>-1</sup>. If the selection rules in group theory are followed, the peak at 133 cm<sup>-1</sup> corresponds to the  $E_g^2$ 

mode, whereas the other two peaks at 75 cm<sup>-1</sup> and 175 cm<sup>-1</sup> have to be assigned to the first and second order  $A_{1g}$  modes respectively. On the other hand, the peak at ~105 cm<sup>-1</sup> corresponds to  $E^{I}_{u}$  mode. The letter A designates the out-of-plane lattice vibrations whereas the letter *E* signifies the in-plane ones. Raman active modes are denoted by the subscript "*g*" while "*u*" is for the infrared active modes. The Bismuth atoms are designated as Bi and the outer Se atoms of a quintuple layer are designated as Se1 and the inner ones are designated as Se2. The observed frequencies resemble with the earlier reported phonon vibrational modes of Bi<sub>2</sub>Se<sub>3</sub> [25].



**Figure 4.1.** (*a*) X-ray diffraction pattern of  $Cu_{0.13}Bi_2Se_3$  single crystal and inset shows photographs of as grown and cleaved  $Cu_{0.13}Bi_2Se_3$  single crystals, (*b*) Rietveld Refinement of powder XRD patterns of  $Cu_xBi_2Se_3$  (*x* = 0, 0.13, 0.25) samples, (*c*) Raman Spectra of  $Cu_xBi_2Se_3$  samples (*d*) shift of  $A^2_{1g}$  peak in Raman spectra. FESEM images of single crystals of (*e*)  $Bi_2Se_3$  (*f*)  $Cu_{0.13}Bi_2Se_3$  and (*g*)  $Cu_{0.25}Bi_2Se_3$ .

With Cu-intercalation,  $A_{1g}^2$  mode vibrational peak shifts towards lower energy as shown in Fig. 4.1 (*d*). Since the  $A_{1g}^2$  mode corresponds to the out of plane vibrations of Bi and Se1 atoms along the *c*-direction, the Cu intercalation ease the vibration of Bi atoms away from Se1 by attracting them thus the Bi atoms have to spent less energy which correspond to lower energy Raman peaks [23]. But in case of *x*=0.25, the Cu atoms (with smaller atomic radius) start replacing Bi atoms (with larger atomic radius) from their sites which decreases the total length of the Bi<sub>2</sub>Se<sub>3</sub> molecule and creates more void space for the vibration of the atoms. Now the Cu atoms need more energy to vibrate which correspond to higher energy Raman Peak at 175.63 cm<sup>-1</sup> but still less than pure Bi<sub>2</sub>Se<sub>3</sub> 176.48 cm<sup>-1</sup>) because only few amount of Bi has been replaced. An IR active mode at 105 cm<sup>-1</sup> was observed in both the crystals due to quantum size effects [26].

## 4.3.3. Humidity Sensing

#### 4.3.3.1. Measurement Setup

As per previous reports ITO coated glass substrates of dimension 1 cm × 1 cm were used for device fabrication [18-20, 27]. Humidity sensors were prepared using single crystals of pure and Cu intercalated Bi<sub>2</sub>Se<sub>3</sub> samples. Saturated solutions of inorganic salts like KOH (8%), MgCl<sub>2</sub>.6H<sub>2</sub>O (33%), K<sub>2</sub>CO<sub>3</sub> (43%), Mg(NO<sub>3</sub>)<sub>2</sub> (52%), NaNO<sub>3</sub> (63%), NaCl (75%), KCl (86%) and K<sub>2</sub>SO<sub>4</sub> (97%) were utilized to create an ambient system at room temperature with particular amount of humidity [28]. The sensing properties characterized by the variation of resistance with time (R-t) of the Cu<sub>x</sub>Bi<sub>2</sub>Se<sub>3</sub> single crystals were measured at different relative humidity. The device under test (DUT) was fixed on a seal made of rubber inside a controlled humidity chamber. The DUT is attached to an external power source in the form of Keithley 2401 source meter and the measurements are recorded through LABVIEW<sup>®</sup> programming.

#### 4.3.3.2. Sensitivity

For transient response measurement, initially the DUT (here  $CuxBi_2Se_3$ ) was preserved in a container with RH of 97%, to attain a steady response, after which it was quickly switched to another RH% container. The switching time was kept very low of 1-2 sec. to minimize any possible interference during the measurement. To establish possible commercial utility, the humidity sensing measurements were done within a relative humidity of 8–97% at bias voltage of 5V. The resistance and sensitivity factor as a function of relative humidity is shown in Fig. 4.2 (*a* and *b*), the error bars shown in the figure were calculated from the differences in resistance and sensitivity obtained at all RH conditions under the same set of experimental conditions. The sensitivity factor of  $Bi_2Se_3$  and Cu intercalated  $Bi_2Se_3$  based humidity sensor were evaluated by using following formula:

$$S(\%) = \frac{R_{08\%} - R_{\Delta R\%}}{R_{\Delta R\%}} \times 100$$
 (5.1)

where, S (%) is sensitivity,  $R_{08\%}$  and  $R_{\Delta R\%}$  are the resistance of the device at lower humidity (8%) and after the change in humidity respectively [23-26]. It is observed that  $Cu_{0.25}Bi_2Se_3$  shows sensitivity value of ~849% which is nearly 6 and 3.45 times higher than that of  $Bi_2Se_3$  and  $Cu_{0.13}Bi_2Se_3$ , respectively. A well-defined table comprising of the comparative study of operable humidity range, sensitivity as well as response and recovery time with available literatures based on metal oxides, metal dichalcogenides and carbon based materials have been included in the Table 4.2.

**Table 4.2.** Comparative analysis of Cu intercalated  $Bi_2Se_3$  TI humidity sensor in terms of linear range, sensitivity and response-recovery time with available literatures.

Material	Linear Range (%)	Sensitivity	Response/ Recovery Time (s)	Refer ence
ZnO nanowires	25 to 90	184	NA	[29]
MoS <sub>2</sub> film	13 to 83	16.08 (p) 89.66 (n)	55s/288s 174s/345s	[30]
SnO <sub>2</sub> :Sn composite thin film	11 to 95	265	80s/140s	[31]
CuO nanowires	20 to 90	12.72%	NA	[32]
Porous titania ceramics	11 to 95	~10 <sup>4</sup>	32s/131s	[33]
ZnO nanosheets	12 to 96	220	600s/3s	[34]
Sn-doped ZnO nanorod Arrays	40 to 90	3.41	230s/30s	[35]
ZnO nanorods	33 to 95	61.23	NA	[36]
SnO <sub>2</sub> Nanowire	5 to 85	32	120s/20s	[37]
WS <sub>2</sub> /WSe <sub>2</sub> Nanohybrids	40 to 80	57	40s/65s	[38]
Fe <sub>2</sub> O <sub>3</sub> /SiO <sub>2</sub> composites	11 to 95	10 <sup>4</sup>	20s/40s	[39]
WS <sub>2</sub> nanosheets	40 to 80	37.5	13s/17s	[40]
NiO–SnO <sub>2</sub> nanofibers	0 to 100	83	22s/44s	[41]
Polyaniline/WS <sub>2</sub> composite	10 to 97	88.46	56s/70s	[42]
rGO/MoS <sub>2</sub> hybrid composites	10 to 90	49	17s/474s	[43]
Single crystalline ZnO nanowire	10 to 90	88	60s/3s	[44]

Cu <sub>x</sub> Bi <sub>2</sub> Se <sub>3</sub>	8-97	849	24 s/25 s	This work
CoFe <sub>2</sub> O <sub>4</sub> nanoparticles	8-97	~590	25/2.6 s	[59]
Zn <sub>1-x</sub> Ni <sub>x</sub> O nanostructures	33-97	152	27/3 s	[58]
SnSe nanorods	11-97	~100	68/149s	[57]
VS <sub>2</sub> nanosheets	0 to 100	~325	40s/50s	[56]
WS <sub>2</sub> spherical nanoparticle	11 to 97	469	12s/13s	[55]
MoS <sub>2</sub> Nanosheets	10 to 60	~3	9s/17s	[54]
MoS <sub>2</sub> Thin Film	25 to 40	5.5	250s/250s	[53]
WO <sub>3</sub> -SnO <sub>2</sub> nanospheres	35 to 98	16.2	8s/29s	[52]
graphene/TiO <sub>2</sub> composites	12 to 90	10 <sup>2</sup>	128s/68s	[51]
ZnO nanocrystals	5 to 85	150	50s/6s	[50]
TiO <sub>2</sub> thin film	11 to 97	~10 <sup>2</sup>	10s/176s	[49]
TiO <sub>2</sub> nanowires /Nafion	12 to 97	>1000	<120s/<120 s	[48]
TiO <sub>2</sub> nanotubes	11 to 95	~57	100s/190s	[47]
WS <sub>2</sub> /GO Nanohybrids	40 to 80	0.044/%RH	25s/29s	[46]
mesoporous TiO <sub>2</sub>	9 to 90	10 <sup>5</sup>	24s/400s	[45]
Caland				

As it can be seen from Fig. 4.2 (*a*), the resistance of all the sensors prepared using pure Bi<sub>2</sub>Se<sub>3</sub>, Cu<sub>0.13</sub>Bi<sub>2</sub>Se<sub>3</sub> and Cu<sub>0.25</sub>Bi<sub>2</sub>Se<sub>3</sub> samples decreases with increasing relative humidity which infers the increase in sensitivity as shown in Fig. 4.2 (b). Fig. 4.2 (c) shows the best lines fitted to the experimental data attaining high linear coefficient of  $R^2 = 0.96$ , 0.97 and 0.96 for the sensor made by using pure Bi<sub>2</sub>Se<sub>3</sub>, Cu<sub>0.13</sub>Bi<sub>2</sub>Se<sub>3</sub> and

Cu<sub>0.25</sub>Bi<sub>2</sub>Se<sub>3</sub>, respectively. The value of the slope increases from 0.08577 to 0.05682 and 0.05349, respectively by increasing the Cu dopant concentration from 13% to 25% in Bi<sub>2</sub>Se<sub>3</sub> which implies increased sensitivity by Bi<sub>2</sub>Se<sub>3</sub> sensor sample. The best lines fitted to the experimental data showed high linear coefficient of  $R^2 = 0.96$ , 0.97 and 0.96 for the sensor made by using pure Bi<sub>2</sub>Se<sub>3</sub>, Cu<sub>0.13</sub>Bi<sub>2</sub>Se<sub>3</sub> and Cu<sub>0.25</sub>Bi<sub>2</sub>Se<sub>3</sub>, respectively. The negative slope value increases from 0.08577 to 0.05682 and 0.05349 respectively by increasing the Cu dopant concentration from 13% and 25% in Bi<sub>2</sub>Se<sub>3</sub> which implies increased sensitivity by Bi<sub>2</sub>Se<sub>3</sub> sensor sample. The increase in sensitivity of Cu intercalated Bi<sub>2</sub>Se<sub>3</sub> than that of pure Bi<sub>2</sub>Se<sub>3</sub> (Cu<sub>0</sub>Bi<sub>2</sub>Se<sub>3</sub>) can be ascribed to the band bending effect which is induced by water molecule adsorption over the surface. Due to band bending a shift in Dirac point into occupied state, an increase in the charge carriers at the surface causes decreased resistance with increase of humidity level [60-62].



**Figure 4.2.** (*a*) Resistance *vs.* % RH, (*b*) Sensitivity *vs.* % RH and (*c*) Linear Analysis of resistance vs. percent relative humidity, (*d*) Hysteresis of  $Cu_xBi_2Se_3$  (*x*= 0,0.13,0.25) samples within 8-97% RH.

### 4.3.3.3. Hysteresis Behaviour

In order to demonstrate the hysteresis behaviour, the variation of resistance of the sensor devices made of pure and Cu intercalated Bi<sub>2</sub>Se<sub>3</sub> single crystals were recorded. The resistance through the device was measured at various humidity levels (with increasing humidity from 8% to till 97% and then decreasing it back to 8% again). Hysteresis is the resistance drift observed by the device during operational cycle at any RH value. The hysteresis generally arises due to the adsorption and desorption processes for various levels of humidity. From Table 4.3, it can be seen that the hysteresis values are quite small for most of the humidity levels.

**Table 4.3.** Hysteresis values of pure and Cu intercalated Bi<sub>2</sub>Se<sub>3</sub> (Cu<sub>0</sub>Bi<sub>2</sub>Se<sub>3</sub>, Cu<sub>0.13</sub>Bi<sub>2</sub>Se<sub>3</sub> and Cu<sub>0.25</sub>Bi<sub>2</sub>Se<sub>3</sub>) at different levels of % RH.

RH%	Bi <sub>2</sub> Se <sub>3</sub>	Cu0.13Bi2Se3	Cu <sub>0.25</sub> Bi <sub>2</sub> Se <sub>3</sub>
8	0.00177	0.00021	0.00050
33	0.00188	0.00966	0.00117
43	0.00212	0.00318	0.00133
52	0.00070	0.00546	0.00104
63	0.00377	0.00028	0.00084
75	0.00396	0.00693	0.00079
86	0.00115	0.00481	0.00048
97	0.00041	0.00021	0.00023

The hysteresis error in humidity sensors were calculated using the expression,

$$H_{\rm e} = \pm \frac{\Delta R_{max}}{2F_{FS}} \tag{5.2}$$

Where  $\Delta R_{max}$  is the difference of resistance between adsorption modes and desorption modes whereas  $F_{FS}$  is the output of full-scale [18-20, 27]. Fig. 4.2 (*d*) shows that the adsorption- desorption curves for Cu<sub>x</sub>Bi<sub>2</sub>Se<sub>3</sub> (x = 0, 0.13, 0.25) TI humidity sensors. It is observed that pure Bi<sub>2</sub>Se<sub>3</sub> shows maximum hysteresis error value around 0.00396 at 75% RH. Whereas, the Cu<sub>0.13</sub>Bi<sub>2</sub>Se<sub>3</sub> and Cu<sub>0.25</sub>Bi<sub>2</sub>Se<sub>3</sub> samples show maximum hysteresis of about 0.00966 at 33% RH and 0.00133 at 43% RH, respectively. The above result confirms practical feasibility of the Bi<sub>2</sub>Se<sub>3</sub> topological insulators as humidity sensors showing very negligible value of hysteresis during the operational period, highly desirable for devices.

#### 4.3.3.4. Freundlich Adsorption Isotherm Modelling

Relative deviation in Resistance (R.D.R or  $\Delta R_H$ ) indicates the variation in resistance during operation of the **D**evice Under Test (DUT) between different RH environments. The relative deviation in resistance ( $\Delta R_H$ ) values was calculated for the samples by using following expression [18-20, 27]:

$$\Delta R_{\rm H} (\%) = (R_{\rm LH} - R_{\rm H}) / R_{\rm LH} \times 100\%$$
(5.3)

Where,  $R_{LH}$  and  $R_H$  are the sample resistance at lowest RH (i.e. 8% RH) and that of other relative humidity values. For pure and Cu intercalated Bi<sub>2</sub>Se<sub>3</sub> humidity sensor samples,  $\Delta R_H$  against relative humidity plot doesn't show linearity (Fig. 4.3 (a)) which is associated with the conduction mechanism. The conduction process was ascribed to chemisorbed layers and physisorbed layers before and after transition point ( $T_c$ ), respectively. The plots of RDR *vs.* % RH show different slopes for two different regions, justifying the idea of calibration of sensor devices to the electronic circuits. Hence lowering the value of  $T_c$  is another aspect for improvement of commercial deployment of sensors for real time monitoring. The variation in RDR is shown in Fig. 4.3 (*a*), where the Bi<sub>2</sub>Se<sub>3</sub>, Cu<sub>0.13</sub>Bi<sub>2</sub>Se<sub>3</sub> and Cu<sub>0.25</sub>Bi<sub>2</sub>Se<sub>3</sub> samples shows  $\Delta R_H$  value up to 58%, 83% and 89%, respectively from their initial resistance values. In order to know the conduction process and the application of topological insulators as humidity sensors, here we utilize adsorption isotherm like Freundlich adsorption isotherm model. The model was utilized to explain the relationship between humidity sensing within a RH range and the plausible mechanism of humidity sensing. In case of humidity sensing, surface active groups are attached to adsorbed water molecules through hydrogen bonds. The reversibility observed during humidity sensing can be ascribed as a surface phenomenon which is taking place over the surface and within the single crystal. In general, the Freundlich isotherm curve relates the concentrations of solute on the surface of an adsorbent (adsorbed oxygen on the surface of experimented sample *i.e.* Bi<sub>2</sub>Se<sub>3</sub>, Cu<sub>0.13</sub>Bi<sub>2</sub>Se<sub>3</sub> and Cu<sub>0.25</sub>Bi<sub>2</sub>Se<sub>3</sub>) and the solute concentration (water vapour).



**Figure 4.3.** (*a*) Relative deviation in Resistance (RDR or  $\Delta R_{\rm H}$ ) vs. percent relative humidity of pure and Cu intercalated Bi<sub>2</sub>Se<sub>3</sub> topological insulators. Log-log plot of measured and modelled (Freundlich) behaviour of Relative Deviation in resistance ( $\Delta R_{\rm H}$ ) vs. percent relative humidity of (*b*) Bi<sub>2</sub>Se<sub>3</sub>, (*c*) Cu<sub>0.13</sub>Bi<sub>2</sub>Se<sub>3</sub> and (*d*) Cu<sub>0.25</sub>Bi<sub>2</sub>Se<sub>3</sub> samples.

The isotherm is expressed as:
$$S = \kappa * (RH)^{\alpha} \tag{5.4}$$

Where S is the relative deviation in resistance, k is adsorption capacity, RH is the relative humidity percentage and  $\alpha$  referred to the adsorption strength, respectively [18-20, 27, 63]. To the best of our knowledge, it is indeed the first attempt to model Freundlich adsorption isotherm for any topological insulator based humidity sensors to investigate the uptake of water vapour during the sensing process and the mechanism behind it.

Fig. 4.3 (*b-d*) shows linear fitting of experimental water adsorption data in two separate regions with distinct linearity within the range of entire RH. Both the regions of low RH (8%-52%) as well as the high RH (52%-97%) are concomitant with regimes of different adsorption. The point of transition ( $T_c$ ) is obtained from the point where the two linear fits coincide. From Fig. 4.3 (*b-d*) the  $T_c$  value was found to be 50.96% RH, 33.34% RH and 16.78% RH for Bi<sub>2</sub>Se<sub>3</sub>, Cu<sub>0.13</sub>Bi<sub>2</sub>Se<sub>3</sub> and Cu<sub>0.25</sub>Bi<sub>2</sub>Se<sub>3</sub>, respectively. The linear fitting of each individual region is done in accordance to the Freundlich model. The constants  $\alpha$  and k are determined from the fitting and shown in Table 4.4 for all Cu<sub>x</sub>Bi<sub>2</sub>Se<sub>3</sub> samples.

**Table 4.4.** Freundlich adsorption isotherm model results, including adsorption capacity (*k*), adsorption strength ( $\alpha$ ), and R<sup>2</sup> values vs. the experimental data for humidity sensing using Bi<sub>2</sub>Se<sub>3</sub>, Cu<sub>0.13</sub>Bi<sub>2</sub>Se<sub>3</sub> and Cu<sub>0.25</sub>Bi<sub>2</sub>Se<sub>3</sub>.

Sample	Low RH Regime			High RH Regime		
	k	α	$R^2$	k	α	<b>R</b> <sup>2</sup>
Bi <sub>2</sub> Se <sub>3</sub>	1.03±0.06	1.72±0.14	0.96	1.32±0.27	0.40±0.04	0.97
Cu <sub>0.13</sub> Bi <sub>2</sub> Se <sub>3</sub>	2.31±0.29	1.22±0.16	0.87	1.46±0.31	0.66±0.09	0.92
Cu <sub>0.25</sub> Bi <sub>2</sub> Se <sub>3</sub>	4.3±0.19	0.91±0.08	0.92	3.03±0.16	0.87±0.02	0.95

It is reported that higher  $\alpha$  value shows stronger adsorption in the specific RH regime. It has been observed from Fig. 4.3 (b-d) that adsorption intensification ( $\alpha$ ) value of pure Bi<sub>2</sub>Se<sub>3</sub> and its Cu intercalated (Cu<sub>0.13</sub>Bi<sub>2</sub>Se<sub>3</sub>

and  $Cu_{0.25}Bi_2Se_3$ ) counterpart's shows opposite trend in both low and high RH region as shown in Fig. 4.4 (*a*). The calculated *k* value signifies the capacity of water adsorption at particular RH state and calculated *k* values are represented in Fig. 4.4 (b). This confirms a higher water vapour adsorption capacity of  $Cu_{0.13}Bi_2Se_3$  sample than that of  $Cu_{0.25}Bi_2Se_3$  for better performance.



**Figure 4.4.** (*a*) Variation of adsorption intensification ( $\alpha$ ) with Cu content (%) (b) variation of adsorption capacity (*k*) as a function of Cu content in Bi<sub>2</sub>Se<sub>3</sub>.

The  $\alpha$  values for Bi<sub>2</sub>Se<sub>3</sub>, Cu<sub>0.13</sub>Bi<sub>2</sub>Se<sub>3</sub> and Cu<sub>0.25</sub>Bi<sub>2</sub>Se<sub>3</sub> are found to be 1.72,1.22 and 0.91 in low RH region whereas the value shows an increment from 0.40, 0.66 and 0.87 in high RH region. Table 4.4 and fig. 4.4 (*a*) show that Cu<sub>0.25</sub>Bi<sub>2</sub>Se<sub>3</sub> shows comparable  $\alpha$  value in both low (8-52%) and high (52-97%) RH region makes it more reliable TI candidate for its operation over the subjected RH regime. Similarly, a correlation between adsorption capacities (*k*) with Cu content in Bi<sub>2</sub>Se<sub>3</sub> is shown in Fig. 4.4 (*b*). It is observed that in both low and high RH regions an increase in *k* value is observed with increase in Cu content indicates stronger intermolecular interactions between adsorbate and adsorbent. The overall results obtained from Freundlich model suggests that among all the samples Cu<sub>0.25</sub>Bi<sub>2</sub>Se<sub>3</sub> shows a consistent performance in terms of adsorption capacity (*k*) and strength ( $\alpha$ ) within the 8-97% RH region. Due to minimal variation in fitting parameters (*k* and  $\alpha$ ) from the isotherm in both low and high RH concludes effectively faster and smoother adsorption-desorption of water vapour over the surface enhances humidity sensing of Cu<sub>0.25</sub>Bi<sub>2</sub>Se<sub>3</sub> sample. Generally, water vapour in different relative humidity directly interact with transition metal (TM) doped or intercalated topological insulators like Bi<sub>2</sub>Se<sub>3</sub> modify resistance and sensing takes place in chemi-resistive humidity sensors. From the above discussion it has been suggested that the humidity sensing properties can improve by introducing doping or intercalation into topological insulators, as variation in RH values shows stronger adsorption affinity towards them.

#### 4.3.3.5. Langmuir Adsorption (LA) Isotherm Analysis

When the Bi<sub>2</sub>Se<sub>3</sub> based topological insulator humidity sensors are exposed to varied RH values, it reacts with chemisorbed oxygen species, resulting in lowering of potential barrier which leads to the increase in sensitivity. Here in the present work it is assumed that the sensitivity is proportional to the relative humidity percentage. If monolayer coverage of humidity is assumed at constant temperature (*T*), then for single adsorption site Langmuir adsorption model, the equation can be expressed as [64],

$$y = Ae^{\left(\frac{\% RH}{x}\right)} + B \tag{5.5}$$

Where B is the base resistance of the sensing material and x is the characteristic RH constant. The sensor transients are analysed using the equation (3) for pure and Cu intercalated Bi<sub>2</sub>Se<sub>3</sub>. The experimental and fitted results are shown in Fig. 4.5. Here a fitting with R<sup>2</sup> values ~ 0.97 is observed and the values of x (characteristic RH constant) values are extracted.

In equation 5.5 the effective number of energetically different adsorption sites and their individual contributions were represented by the number of terms and coefficients, respectively. Here in this case existence of only one effective adsorption site in the material is confirmed from the fitting equation which contains only one exponential term [65]. Typical results of

 $Bi_2Se_3$  and Cu intercalated  $Bi_2Se_3$  sensors exposed repeatedly to particular RH percent shows increase in sensitivity value due to improved conduction of water vapour over the surface. The obtained result was modelled with the above stated Langmuir adsorption isotherm which shows an increased sensitivity with increasing RH% and following equations for Cu<sub>0</sub>Bi<sub>2</sub>Se<sub>3</sub>, Cu<sub>0.13</sub>Bi<sub>2</sub>Se<sub>3</sub> and Cu<sub>0.25</sub>Bi<sub>2</sub>Se<sub>3</sub> were obtained,

$$S = 11.21 \cdot \exp\left[\frac{RH\%}{37.22}\right] - 14.96 \text{ (For Bi}_2\text{Se}_3\text{)}$$
(5.6)

$$S = 13.25 \cdot \exp\left[\frac{RH\%}{26.22}\right] - 22.00 \text{ (For Cu_{0.13}Bi_2Se_3)}$$
(5.7)

$$S = 2.31 \cdot \exp\left[\frac{RH\%}{16.17}\right] - 15.19 \quad (For Cu_{0.25}Bi_2Se_3) \tag{5.8}$$

Here it is observed that the characteristic RH constant (x) denotes a decrease with increase of Cu content confirms improved sensing behaviour in topological insulator.

#### 4.3.3.6. Stability of Humidity Sensors

Fig. 4.6 shows the stability over a long period of time for  $Cu_xBi_2Se_3$  (x=0, 0.13, 0.25) TI humidity sensors to assess the practical applicability. For this purpose, the resistance of the humidity sensor was measured at different humidity with the time being varied from 10 days to 60 days. The average resistance variation over the period lies within permissible limit. From Fig. 4.6 (*a-c*), the variation of maximum average resistance calculated for Bi<sub>2</sub>Se<sub>3</sub>, Cu<sub>0.13</sub>Bi<sub>2</sub>Se<sub>3</sub> and Cu<sub>0.25</sub>Bi<sub>2</sub>Se<sub>3</sub> samples were 118.8 m $\Omega$ , 36.24 m $\Omega$  and 5.2 m $\Omega$  respectively. This result indicates improved sensing property of Cu intercalated Bi<sub>2</sub>Se<sub>3</sub> TI humidity sensors by lowering the resistance variation. This long term stability study establishes usage of Bi<sub>2</sub>Se<sub>3</sub> topological insulators for feasible and much efficient humidity sensor fabrication.

#### 4.3.3.7. Response-Recovery Analysis

Fig. 4.7 (*a-c*) shows the transient resistance behaviour of pure and Cu intercalated Bi<sub>2</sub>Se<sub>3</sub> TIs with varied %RH levels in room temperature. The

measured resistance at 08 RH% is set as reference. The cyclability behaviour study of all the prepared TI humidity sensors were repeated for number of times. The response ( $T_{res}$ ) and recovery ( $T_{rec}$ ) time is defined as the time taken by the sensor to achieve 90 % of resistance change in case of water adsorption and desorption, respectively.



**Figure 4.5** Comparison of sensor response to humidity on an interval of 10 days and Langmuir adsorption isotherm fitting of (*a*)  $Bi_2Se_3$ , (*b*)  $Cu_{0.13}Bi_2Se_3$  and (*c*)  $Cu_{0.25}Bi_2Se_3$  humidity sensors.



**Figure 4.6.** Stability Test for (*a*) pure  $Bi_2Se_3$ , (*b*)  $Cu_{0.13}Bi_2Se_3$  and (*c*)  $Cu_{0.25}Bi_2Se_3$  humidity sensors.



**Figure 4.7.** Transient response/recovery performance during 08%-97%-08% relative humidity cycle for (*a*) pure Bi<sub>2</sub>Se<sub>3</sub>, (*b*) Cu<sub>0.13</sub>Bi<sub>2</sub>Se<sub>3</sub> and (*c*) Cu<sub>0.25</sub>Bi<sub>2</sub>Se<sub>3</sub>, (*d*) response/recovery time of all Bi<sub>2</sub>Se<sub>3</sub> samples.



**Figure 4.8.** Schematic diagram of humidity sensing mechanism in Bi<sub>2</sub>Se<sub>3</sub> topological insulator based humidity sensors.

The response/recovery time for pure Bi<sub>2</sub>Se<sub>3</sub>, Cu<sub>0.13</sub>Bi<sub>2</sub>Se<sub>3</sub> and Cu<sub>0.25</sub>Bi<sub>2</sub>Se<sub>3</sub> samples were found to be 31.8s/32s, 32s/32.27s and 24s/25s. The transient sensing cycles shown in Fig. 4.7 (*a-c*) were found to be repeatable over more than six iterative cycles and continued for several cycles after this event with very narrow deviation in characteristic response/recovery time. So, it can be concluded that Bi<sub>2</sub>Se<sub>3</sub> based topological insulator humidity sensors can be reusable over a number of times which is very important for fabricating such type of devices for the commercial application. The transient response behaviour of all the pristine and Cu intercalated Bi<sub>2</sub>Se<sub>3</sub> samples are in well accordance to their observed long term stability characteristic which estimates the potential performance of the humidity sensor.

#### 4.3.3.8. Humidity Sensing Mechanism

Bi<sub>2</sub>Se<sub>3</sub>, a well-known TI material at room temperature due to the presence of surface metallic states with single Dirac cone even at room temperature and/or at zero magnetic fields can also be classified as a semiconductor at room temperature due to a comparative large bulk band gap of 0.3 eV. Again Bi<sub>2</sub>Se<sub>3</sub> shows dominated charged selenium vacancies as defect in the lattice which generally acts as electron donors result its *n*-type behavior [17, 66]. Hence a possible mechanism which explains qualitatively the humidity sensing properties of topological insulators like Bi<sub>2</sub>Se<sub>3</sub> is proposed hereafter as shown in Fig. 4.8. Generally, due to the presence of little oxygen vacancies in Bi<sub>2</sub>Se<sub>3</sub> TIs, the increase in sensitivity with increasing RH can't be fully assigned to the chemisorption of water molecules on the surface of crystals where water related electrolytic conduction drives the mechanism. At low humidity, presence of few water molecules doesn't show continuous surface coverage causing the electrolytic conduction not fast enough due to which increase in sensitivity is poor. Whereas in high humidity continuous water layers created over the surface increase number of physisorbed layers and hence protonic conduction becomes faster. The domination of strong protonic conduction along with weak electrolytic conduction hence increases the sensitivity of TIs much higher than that of lower humidity condition. The increase in sensitivity of Cu intercalated Bi<sub>2</sub>Se<sub>3</sub> can be ascribed to the fact of increase in number of active sites taking part in water adsorption in the overall RH regime.

## 4.4. Summary

In this chapter, we demonstrate the humidity sensing behaviour of single crystals of  $Cu_xBi_2Se_3$  (x = 0, 0.13 and 0.25) topological insulators. The sensitivity of  $Cu_{0.25}Bi_2Se_3$  crystal sensors in response to relative humidity tuned to a value of 849% proves enhancement in sensing behaviour with intercalation of Cu in pure  $Bi_2Se_3$ . Moreover, other sensing characterizations like low hysteresis and  $T_c$  value (16.78%) with fast

response/recovery time of 24s/25s. proposes TIs as ideal material for humidity sensors. The feasible sensing phenomenon is also associated with the Freundlich adsorption model for a conclusive guiding mechanism. The modelled data shows that for Cu<sub>0.25</sub>Bi<sub>2</sub>Se<sub>3</sub> the water adsorption capacity (*k*) value increases nearly 4 and 2.3 times than that of Bi<sub>2</sub>Se<sub>3</sub> in low and high humidity region, respectively. This confirms increment in number of active sites on surface of TIs which in turn reflected in sensitivity result. Langmuir isotherm model confirms the contribution of adsorption sites over the test period, concluding proportional relationship between sensitivity and humidity. This overall investigation of humidity sensing properties along with theoretical insight thus proposes high possibility and immense potential of Bi<sub>2</sub>Se<sub>3</sub> based TIs for fabrication of multifunctional high performance humidity sensors feasible in near future.

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## **Chapter 5**

# Enhanced Field Emission Properties of Ni Doped Bi<sub>2</sub>Se<sub>3</sub> Nanomaterials

In recent decades, nanostructured materials have attracted considerable attention due to their enhanced field electron emission (FE) performances but have limited applications due to degraded surface states which decreases the emission rate. In this respect, the topological surface states protecting materials may be of significant use for such FE applications. This chapter explores the FE properties of nanostructures of Bi<sub>2</sub>Se<sub>3</sub> and Ni doped Bi<sub>2</sub>Se<sub>3</sub> samples prepared by a hydrothermal method. An enrichment in the FE properties in terms of the threshold and turn-on field values of Ni doped Bi<sub>2</sub>Se<sub>3</sub> was determined. Experimental results signify many prospects for potential applications of Ni doped Bi<sub>2</sub>Se<sub>3</sub> in emission based devices.

## **5.1.** Background of the Work

Semiconductor materials having nanostructures recently gained much attention due to their plethora of advanced electronic, structural, optical as well as thermal properties and multi-faceted applications such as photovoltaic devices, sensors, catalysts, etc. Also over the last decade topological insulators (TI) are emerged as the pioneering candidate for research and development in theoretical as well as experimental physics due to their potential application in quantum computing and spintronic devices [1]. They are defined as the materials which are insulating in the bulk but boast of conducting surface states topologically protected by time reversal symmetry [2, 3]. Bi<sub>2</sub>Se<sub>3</sub> is one of the only few renowned materials which can be classified as a semiconductor as well as a TI at room temperature because not only it has a large bulk band gap of 0.3 eV and simple surface state structure with single Dirac cone (even at room temperature and/or zero magnetic field) [4] but also has defect chemistry in the lattice structure dominated by charged selenium vacancies, which act as electron donors [5], resulting in n type behaviour of Bi<sub>2</sub>Se<sub>3</sub>. Various experimental techniques have been conducted to probe the topological surface states resulting in considerable amount of progress on the electrical transport properties of Tis [6-9]. Difficulty (arising from the bulk carriers instigating from the Se vacancy while synthesizing) in studying the surface state properties of TI by transport measurements is an old thought now since surface to bulk coherent coupling [10], exchange coupling induced symmetry breaking in Dirac surface states [11] and electrostatic coupling between two surface states of a TI [12] are discovered and experimentally verified also. Some crucial information about the electronic states can be known from the quantum tunnelling of the electrons from the material surface into the vacuum. Field electron emission is a phenomenon comprises of extracting of electrons from the surface of a material by means of quantum tunnelling through the potential barrier at the surface in the influence of a strong

electric field. Modern day applications are high energy accelerators, vacuum microelectronic devices and microwave amplifiers [13-15]. One dimensional (1D) nanomaterials like Carbon nanotubes, ZnO nanowires [16-20] in addition with two dimensional materials such as graphene [21-24] and MoS<sub>2</sub> [25] have been studied for the last few years depicting an outstanding FE property of single layer graphene. With a single Dirac cone dispersion relation, the surface state of Bi<sub>2</sub>Se<sub>3</sub> has an electronic structure analogous to graphene, inspiring us to revisit the FE properties of Bi<sub>2</sub>Se<sub>3</sub> nanostructures. Available literatures on the FE properties of Bi<sub>2</sub>Se<sub>3</sub> are extremely scarce. Poor field electron emission from the surface of Bi<sub>2</sub>Se<sub>3</sub> was observed by Yan et al [26]. The reason behind this was oxidation at the surface when exposed to the atmosphere. Oxidation causing due to cold electron emission can degrade the FE performances of well-known field emitters [27]. For producing a FE device, the major challenge is to protect the surface of the field emitters from degradation when subjected to a high electric field. Topological insulator materials protecting their surface states may be of significant use for such FE applications. So far different dimensions of nanostructures like nanorods [28], nanoribbons [29], nanoplatelets [30] and nanodiscs [31] of Bi<sub>2</sub>Se<sub>3</sub> have been synthesized by several ways like electrodeposition [32], vapour liquid solid phase [33], sono-electrochemical deposition techniques [34] and chemical vapour deposition [35] requiring very high deposition temperatures or difficult synthesis set-ups, introducing first-hand financial as well as industrial barriers. Thus a simple, efficient and cost effective two step synthesis route is appropriate. In this work, we report on the synthesis of high quality Bi<sub>2</sub>Se<sub>3</sub> and Ni doped Bi<sub>2</sub>Se<sub>3</sub> nanoflake (NF) arrays with a large area with high-yield by simple two step synthesis route containing chemical bath deposition approach and hydrothermal synthesis. Thorough investigations were carried out on the properties of field electron emission from the surfaces of Bi<sub>2</sub>Se<sub>3</sub> and Ni doped Bi2Se3 nanoflakes into the adjacent vacuum. Our

measurements indicate a remarkable improvement in the FE properties of Bi<sub>2</sub>Se<sub>3</sub> due to nickel doping.

## 5.2. Synthesis Procedure

Bismuth nitrate pentahydrate (Bi(NO<sub>3</sub>)<sub>3</sub>.5H<sub>2</sub>O) (99.99%), Sodium Sulphite (Na<sub>2</sub>SO<sub>3</sub>) (99.99%), Selenium powder (99.99%), Nickel Nitrate Hexahydrate (Ni(NO<sub>3</sub>)<sub>2</sub>, 6H<sub>2</sub>O) (99.99%) were purchased from Sigma Aldrich. Ethylenediaminetetraacetic Acid (EDTA) and Ascorbic Acid were purchased from Alfa Aesar. All chemicals used were of analytical grade and were used as received without any further purification. All of the solutions were prepared with deionized water.

In this usual synthesis process, hierarchical Bi<sub>2</sub>Se<sub>3</sub> NFs were grown using  $(Bi(NO_3)_3.5H_2O)$  and Na<sub>2</sub>SeSO<sub>3</sub> as sources of Bi<sup>3+</sup> and Se<sup>2-</sup>, respectively. In the chemical bath, bismuth chelate was prepared with the solution of 4 ml of 0.1 M Bi(NO<sub>3</sub>)<sub>3</sub>.5H<sub>2</sub>O and 80 ml of 0.1 M EDTA. 4 ml of 0.5 M Ascorbic acid, as a reducing agent, was added to the mixture under constant stirring. The pH was maintained at around 8.5 by adding aqueous ammonia solution drop by drop until the solution turns transparent. In a separate system a 0.1 M Na<sub>2</sub>SeSO<sub>3</sub> solution was prepared by mixing 0.25 M Na<sub>2</sub>SO<sub>3</sub> with 0.1 M Se powder at 80°C with constant stirring for 8 hrs. Then around 8 ml of the nascent Na<sub>2</sub>SeSO<sub>3</sub> solution was added dropwise to the bismuth solution. After vigorous stirring for 30 min, the solution was kept in a 100 ml Teflon liner, sealed in an autoclave and heated at 175°C for 24 hrs. The autoclave was furnace cooled to room temperature. The product was subject to centrifugation at 8000 rpm for 10 min. The resultant material was washed with distilled water and absolute ethanol a number of times to eliminate all of the impurities. After that the solid product was dried in an oven at 70°C for few hours. For Ni doped Bi<sub>2</sub>Se<sub>3</sub> nanostructures, 4 ml of 0.1 M Ni(NO<sub>3</sub>)<sub>2</sub>, 6H<sub>2</sub>O was added to the Bismuth chelate prior to the addition of freshly

prepared Na<sub>2</sub>SeSO<sub>3</sub> solution. All the other procedures were remained as mentioned above

## **5.3.** Results and Discussion

## 5.3.1. Morphological Analysis

Bi<sub>2</sub>Se<sub>3</sub> is a crucial candidate for topological insulator. The surface electronic states which are unique than the bulk, play a crucial role in the transportation of electron. Fig. 5.1 presents the FESEM images of the as synthesized Bi<sub>2</sub>Se<sub>3</sub> and Ni doped Bi<sub>2</sub>Se<sub>3</sub> nanostructures. Both the material exhibits nanoflakes morphologies as shown in the Fig 5.1 (a) and (b) with excellent uniformity. The average length of pure Bi<sub>2</sub>Se<sub>3</sub> nanoflakes was measured to be ~ 550 nm having average thickness of 28 nm. Whereas for Ni doped Bi<sub>2</sub>Se<sub>3</sub> the average length and thickness were measured to be ~ 350 nm and 24 nm, respectively. Nanoflake arrays in pure Bi<sub>2</sub>Se<sub>3</sub> are actually composed of thinner flakes whose widths are larger compared to Ni doped Bi<sub>2</sub>Se<sub>3</sub>. Thus in a unit area higher number of nanoflakes are present when Ni is incorporated in the Bi<sub>2</sub>Se<sub>3</sub> crystal structure.



Figure 5.1. FESEM images of (a) Pure Bi<sub>2</sub>Se<sub>3</sub> and (b) Ni doped Bi<sub>2</sub>Se<sub>3</sub>.

### 5.3.2. Structural Analysis

The XRD pattern is represented in Fig. 5.2. (a). The peaks were indexed to the pure hexagonal structure of  $Bi_2Se_3$  with space group of R-3m (JCPDS 33-0214). It can be seen from the figure that with Ni doping the diffraction

peaks shift to higher 2 $\theta$  values which corresponds to the insertion of nickel at Bi site in Bi<sub>2</sub>Se<sub>3</sub> crystal structure. This results in decrement of the lattice parameter which is in well agreement with the fact that ionic radius of nickel (0.72 Å) is smaller than that of bismuth (1.03 Å). The estimated Ni doping was about 7.5 %, confirmed from EDX. Some NiSe peaks (*e.g.* at 15 and between 30° and 40°, marked with \*) are also appeared in Ni doped Bi<sub>2</sub>Se<sub>3</sub>. Also minute amount of unidentified impurity peak was found at 16° (marked with #). From Williamson-Hall plot, shown in Fig. 5.3 (*a* and *b*) the crystallite size and lattice strain of the synthesized material have been calculated from the intercepts and slopes using the equation - (3.1) [36].

$$\beta\cos\theta = K\frac{\lambda}{D} + 2\varepsilon\sin\theta \tag{3.1}$$

Where  $\beta$  (FWHM) is in radian,  $\theta$  is the angle of diffraction, *K* is the shape factor (0.94),  $\lambda$  is the wavelength of Cu K<sub>a</sub> radiation, *D* is the average crystallite size and  $\xi$  is the value of lattice strain. The average crystallite size and lattice strain of pure Bi<sub>2</sub>Se<sub>3</sub> are ~ 48 nm and 18.5 × 10<sup>-4</sup>, whereas for Ni doped Bi<sub>2</sub>Se<sub>3</sub>, it is ~ 30 nm and 84.4 × 10<sup>-4</sup>, respectively. Fig. 5.4 (*a*) shows the HRTEM image of Ni doped Bi<sub>2</sub>Se<sub>3</sub> nanoflakes. The interplanar spacing was measured to be 0.30 nm corresponding to the (015) plane of Bi<sub>2</sub>Se<sub>3</sub>. SAED pattern in fig. 5.4 (*b*) shows the ring for (015) and (110) planes corresponds to the lattice fringes of 0.30 nm and 0.21 nm, respectively. This confirms the crystalline nature for individual nanoflakes (Fig. 5.4 (a)), which are arranged randomly (Fig. 5.4 (*b*)) of nano-flakes and in good agreement with the earlier reports [37, 38].



**Figure 5.2.** (a) X ray diffraction pattern of Bi<sub>2</sub>Se<sub>3</sub> and Ni doped Bi<sub>2</sub>Se<sub>3</sub>. (b) Atomic model of pure Bi<sub>2</sub>Se<sub>3</sub>.



Figure 5.3. Williamson Hall Plot of (a) Bi<sub>2</sub>Se<sub>3</sub> and (b) Ni doped Bi<sub>2</sub>Se<sub>3</sub>.



**Figure 5.4.** (a)HRTEM image of Ni doped Bi<sub>2</sub>Se<sub>3</sub> nanoflake sample and (b) corresponding SAED pattern.

#### 5.3.3. Field Emission Properties

As Bi<sub>2</sub>Se<sub>3</sub> is a topological insulator its surface states are highly conducting i.e. there are large number of electrons available which can contribute significantly in the field emission of electrons from the sample surface. Fig. 5.5 (a) depicts the variation of field emission current density with respect to the applied electric field of Bi<sub>2</sub>Se<sub>3</sub> and Ni doped Bi<sub>2</sub>Se<sub>3</sub>. The turn on field, defined as the applied electric field resulting in an emission current of 10  $\mu$ A cm<sup>-2</sup>, is a significant parameter for the characterization of FE properties. The turn-on field is observed to be  $3.2 \text{ V} \mu \text{m}^{-1}$  significantly lower (see Table 5.1) as compared to other Bi<sub>2</sub>Se<sub>3</sub> nanostructure [26] and lower than similar kind of Bi<sub>2</sub>Se<sub>3</sub> nanoflakes reported elsewhere [39]. In case of Ni doped  $Bi_2Se_3$  the turn on field is observed to be 1.9 V  $\mu m^{-1}$  lower even than Ni doped ZnO nanostructures [40] as well as Ag decorated Bi<sub>2</sub>Se<sub>3</sub> nanoflakes [39]. This is the first report in Ni doped  $Bi_2Se_3$  field emission. The values of the threshold field needed to generate emission current densities of 100  $\mu$ A cm<sup>-2</sup> were 4.1 V  $\mu$ m<sup>-1</sup> and 2.5 V  $\mu$ m<sup>-1</sup> in case of pure Bi<sub>2</sub>Se<sub>3</sub> and Ni doped Bi<sub>2</sub>Se<sub>3</sub>, respectively. The values for threshold field are also significantly lower than the other reported Bi<sub>2</sub>Se<sub>3</sub> nanostructures as well as decorated ones [26, 39, 40]. A rapid increase in the emission current density was observed when the applied electric field is increased. For Bi<sub>2</sub>Se<sub>3</sub> the observed emission current density was 173 µA cm<sup>-2</sup> when the applied field is 4.4 V  $\mu$ m<sup>-1</sup> whereas for Ni doped Bi<sub>2</sub>Se<sub>3</sub> the current density was 182  $\mu$ A  $cm^{-2}$  with an applied electric field of 2.8 V  $\mu m^{-1}$ .



**Figure 5.5.** Comparative Field Emission Behaviour of Bi<sub>2</sub>Se<sub>3</sub> and Ni doped Bi<sub>2</sub>Se<sub>3</sub> (a) J–E characteristics (b) Corresponding Fowler–Nordheim (F–N) plot of Bi<sub>2</sub>Se<sub>3</sub> (black) and Ni doped Bi<sub>2</sub>Se<sub>3</sub> (red).



**Figure 5.6.** Band diagram of  $Bi_2Se_3$  and Ni doped  $Bi_2Se_3$  nanoflakes with favourable bias conditions for tunnelling. EC – bottom of the conduction band; EF – Fermi level; EV – top of the valance band; the real energy levels for two different electric fields are denoted by solid blue lines.

It is essential to ascertain the reason behind this low turn-on field which is a very promising for technological application. The most probable reason for this low turn on and threshold field can be related to the morphology of our sample because in general the field emission properties vary significantly with the thickness and length of the nanoflakes. The local electric field around the nanoflakes of Ni doped Bi<sub>2</sub>Se<sub>3</sub> is higher than that of the pure one because as shown in the FESEM images (Fig. 5.1.) the average thickness of the nanoflakes for Ni doped Bi<sub>2</sub>Se<sub>3</sub> is 24 nm lower than that of pure Bi<sub>2</sub>Se<sub>3</sub> which is of 28 nm. Field emission is the emission of electric field overcoming the potential barrier by quantum tunnelling. To achieve a good FE property, not only the value of the potential barrier but also the width of the tunnelling barrier should be looked upon. The work function is the energy required to remove an electron from the material to a state at rest in the vacuum nearby the surface, electrons possessing higher energy than that can overcome the potential barrier by itself but those having lower energy still need some push by the electric field to tunnel through the potential barrier [41]. The energy levels with their relative positions in a FE process is schematically given in Fig. 5.6. In no bias mode, the electron need an excess energy to reach the vacuum level. As shown in Fig. 5.6 by the dotted lines, there is a modification on the energy levels in the vacuum with two different applied bias. As a consequence, there is a perturbation in the system raised by the functional bias created by the applied electric field. Due to this now the emitted electron has to tunnel a relatively smaller width of the potential barrier. In this type of system, the real profile of the potential in the influence of the applied field get altered from the ideal situation which one should take into account considering the FE properties. The emitted electron from the barrier tunnelling follows an energy state path that varies with the separation (x) from the cathode, can be termed as:

$$e\phi = e\phi_{work} - \frac{e^2}{16\pi\varepsilon_0 x} - eE_x \tag{3.2}$$

Where  $e \Phi$  is the potential energy of an emitted electron,  $\Phi_{work}$  is the work function and  $\varepsilon_0$  is the permittivity of the material with the applied electric field depicted as *E*. The energy levels when no electric field is applied (*E*<sub>0</sub>) and in the influence of two diverse electric fields *E*<sub>1</sub> (for Bi<sub>2</sub>Se<sub>3</sub>) and *E*<sub>2</sub> (for Ni doped Bi<sub>2</sub>Se<sub>3</sub>) where *E*<sub>1</sub> < *E*<sub>2</sub> and are produced at the interface of the vacuum and Bi<sub>2</sub>Se<sub>3</sub> and Ni doped Bi<sub>2</sub>Se<sub>3</sub> nanostructures. Solid curved blue lines represent the typical plot of equation (2) for two different values of *E*. As mentioned above, the corresponding ideal counterpart was denoted by the dotted slanted violet lines adjacent to these blue lines. Using equation (2), since the height as well as the width of the barrier is smaller in the real situation, shown by the blue solid lines, it will be more favourable for FE. A related point to consider is by applying equal amount of bias voltage over two different sample morphologies one can lead to two different circumstances equivalent to the two electric fields. This can be elaborated as follows. The thinner and smaller nanoflakes present in our sample of Ni doped Bi<sub>2</sub>Se<sub>3</sub> successfully increase the electric field around them owing to their finer structures. Under this circumstances, a similar bias voltage applied over the two samples will generate a larger amount of electric field for samples of Ni doped Bi<sub>2</sub>Se<sub>3</sub> compared to Bi<sub>2</sub>Se<sub>3</sub> where the nanoflakes have higher thickness and size thus producing lower value of electric field. From Fig. 5.6 it is noticeably obvious that, the height and width of the barrier is decreased for a stronger electric field. As a consequence, the electrons will not only have to travel a shorter tunnelling distance but also will need comparatively lower energy in overcoming the barrier in order to emit into the vacuum. To achieve a small value of the turn-on field these two phenomena can play an important as well as cumulative effect for better FE performance. Moreover, larger amount of energy will be possessed by the electrons confined within a strongly enclosed system (as in Ni doped Bi<sub>2</sub>Se<sub>3</sub> nanoflakes of smaller and denser medium) in comparison with a weakly confined system (as in Bi2Se3 nanoflakes of larger size and thickness). Hence to overcome the potential barrier, further a lesser amount of energy is required by the electrons already acquiring higher energies prior to the attraction of an applied electric field. As a result, a threefold constructive perturbation is induced by the variation of morphology in our system containing finer nanoflakes improving the FE properties. The field emission characteristics of Bi2Se3 and Ni doped Bi2Se3 are presented in Table 5.1.

**Table 5.1.** Comparative view of the field emission properties of Bi<sub>2</sub>Se<sub>3</sub> and Ni doped Bi<sub>2</sub>Se<sub>3</sub>.

Serial Number	Sample	Turn-on field (Vμm <sup>-1</sup> ) at 10 μA cm <sup>-2</sup>	Threshold field (Vμm <sup>-1</sup> ) at 100 μA cm <sup>-2</sup>	Max. current density (μAcm <sup>-2</sup> ) at corresponding applied field (V μm <sup>-1</sup> )
1	Bi <sub>2</sub> Se <sub>3</sub>	3.2	4.0	~ 173 at ~ 4.4
2	Ni doped Bi <sub>2</sub> Se <sub>3</sub>	1.9	2.5	~ 182 at ~ 2.8

The obtained J-E curve for the samples shown in Fig. 5.5(*a*) might be more analyzed by the Fowler–Nordheim (FN) theory that can be expressed by the following expression:

$$J = A\left(\frac{\beta^2 E_0^2}{\varphi}\right) exp\left(-\frac{B\varphi^{3/2}}{\beta E_0}\right)$$
(3.3)

where *J* is the field emission current density,  $E_0$  is the applied field between the anode and the cathode,  $\beta$  is the field enhancement factor,  $\varphi$  is the work function, and *A* and *B* are constants ( $A = 1.54 \times 10^{-6} \text{ A eV V}^{-2}$ ,  $B = 6.83 \times 10^3 \text{ V eV}^{-3/2} \,\mu\text{m}^{-1}$ ). Fig. 5.5(*b*) shows the corresponding FN plot ( $\ln(1/E_0^2 \text{ vs } 1/E_0)$ ), which shows a linear relationship for both pure Bi<sub>2</sub>Se<sub>3</sub> and doped ones. The straight line nature of the plot undoubtedly specifies the cold emission behaviour of the materials. Both the materials will have the same value for usual work function (4.3 eV for Bi<sub>2</sub>Se<sub>3</sub> as well as for Ni doped Bi<sub>2</sub>Se<sub>3</sub> as the percentage of Ni doping is too less to alter the work function of Bi<sub>2</sub>Se<sub>3</sub>). But the FN plot of the sample of Ni doped Bi<sub>2</sub>Se<sub>3</sub> exhibits a lower slope than the pristine one. From the slopes of the FN plots one can determine the field enhancement factor ( $\beta$ ), defined as the ratio of the local field to the applied field [42]. The value of the average field enhancement factor for hierarchical Bi<sub>2</sub>Se<sub>3</sub> NFs was obtained as ~ 1.85 x 10<sup>3</sup> whereas for Ni doped hierarchical Bi<sub>2</sub>Se<sub>3</sub> NFs it takes the value ~  $5.69 \times 10^3$ . It is shown by Chen Li *et al.* [43] that  $\beta$  depends on some internal factors such as crystal structure and geometry of the emitter [42], as well as external factors like contribution from the emitters by screening effect, underlying substrate geometry [44] and decorating some metal nanoparticles to modify the emitters that can affect the field enhancement factor. The reason behind the larger  $\beta$  value for Ni doped Bi<sub>2</sub>Se<sub>3</sub> is already discussed earlier.



**Figure 5.7.** The variation of emission current with time at a preset value of 5  $\mu$ A signifying the stability of field emission of (a) Bi<sub>2</sub>Se<sub>3</sub> and (b) Ni doped Bi<sub>2</sub>Se<sub>3</sub> (the insets show the images of the field emission patterns at the stability measurement).

Stability measurements at a constant current of 5  $\mu$ A for a 3 hours' time duration of pure and Ni doped Bi<sub>2</sub>Se<sub>3</sub> samples were studied to understand the stability of the emission as shown in fig. 5.7. A stable performance has been observed maintaining a constant current density which is very crucial for practical applications. The sharp features observed in the graph can depict the adsorption/desorption as well as ion bombardment phenomenon of gas molecules over the solid surface which is generated by a strong electrostatic field, causing fluctuations. The electron emission from the extended edges of the emitters resulting numerous minute spots indicating excellent stability of the material which can be clearly seen in the inset images of fig. 5.7. The FE property of our synthesized material i.e. Ni doped Bi<sub>2</sub>Se<sub>3</sub>, prepared by a two-step synthetic route shows a better performance in terms of turn-on and threshold fields as compared to the other reported  $Bi_2Se_3$  material listed in Table 5.2.

Sample	Synthesis Technique	Turn- on field (Vµm <sup>-1</sup> )	Thresh old field (Vµm <sup>-1</sup> )	β	Ref.
Bi <sub>2</sub> Se <sub>3</sub> nanoflake film	CVD	10.5		172	[26]
Bi <sub>2</sub> Se <sub>3</sub> nanosheets on flexible carbon cloth	Hydrothermal intercalation followed by 3 step exfoliation	2.3		3207	[42]
Layered Bi <sub>2</sub> Se <sub>3</sub> on flat Si	Same as the previous one	2.3		6860	[42]
Hierarchical Bi <sub>2</sub> Se <sub>3</sub> NFs on Si	Chemical Bath Deposition	3.83	7.44	5700	[36]
Ag NPs attached hierarchical Bi <sub>2</sub> Se <sub>3</sub> NFs on Si	Chemical bath deposition under dark condition	2.03	3.67	7200	[36]
ZnO Nanowires	Vapor Deposition at 550°C	6.00	11.00	847	[46]
MoO <sub>3</sub> Nanoflower	Microwave Hydrothermal Method	4.30	7.80	700	[47]
SnS <sub>2</sub> Nanosheets	Hydrothermal Reaction	2.50	5.90		[48]

**Table 5.2.** Comparison of field emission characteristics of  $Bi_2Se_3$  with recent literature of  $Bi_2Se_3$  and commercially used materials.

NiMoO <sub>4</sub> Nanosheets	Facile Hydrothermal Method	2.20	3.20		[49]
In <sub>2</sub> Se <sub>3</sub> Nanowires	Vapor-liquid- solid growth	4.17	6.02	3596	[50]
Bi <sub>2</sub> S <sub>3</sub> Nanowires	Facile Hydrothermal Method	3.08	4.65		[51]
Ag nanowire– rGO composites	Polyol Reflux Technique	5.00		1985	[52]
LaB <sub>6</sub> Nanowire Arrays	Chemical Vapour Deposition	1.82	2.48	1072	[53]
Single- crystalline LaB <sub>6</sub> Nanowires	Catalysis-free Vapor Phase Method	4.62		405	[54]
Bi2Se3 nanoflakes	Bi <sub>2</sub> Se <sub>3</sub> nanoflakes Chemical bath followed by hydrothermal reaction		4.0	1850	This Work
Ni doped Bi2Se3 nanoflakes	Chemical bath followed by hydrothermal reaction	1.9	2.5	5690	This Work

Also the value of the field enhancement factor of Ni doped  $Bi_2Se_3$  nanostructures is quite high (3 times from the pure one), greater than  $Bi_2Se_3$  nanoflakes [26] and nanosheets [45] and within comparable range with layered  $Bi_2Se_3$  [45] and Ag decorated  $Bi_2Se_3$  [36] both on Si substrate.

## 5.4. Summary

In conclusion, Bi<sub>2</sub>Se<sub>3</sub> and Ni doped Bi<sub>2</sub>Se<sub>3</sub> were synthesized by a simple, economical two step synthetic method comprising of chemical bath deposition and hydrothermal synthesis. XRD and SEM results confirm the insertion of Ni ions in Bi<sub>2</sub>Se<sub>3</sub> crystal structure and alterations in the size of the Bi<sub>2</sub>Se<sub>3</sub> nanostructures respectively. Owing to Ni doping, the turn on field of Bi<sub>2</sub>Se<sub>3</sub> decreases from 3.2 V  $\mu$ m<sup>-1</sup> to 1.9 V  $\mu$ m<sup>-1</sup> and the threshold field from 4.0 V  $\mu$ m<sup>-1</sup> to 2.5 V  $\mu$ m<sup>-1</sup>. The maximum current density of 173  $\mu$ A cm<sup>-2</sup> is observed at an applied field of 4.4 V  $\mu$ m<sup>-1</sup> for Bi<sub>2</sub>Se<sub>3</sub> and 182  $\mu$ A  $cm^{-2}$  at an applied field of 2.8 V  $\mu m^{-1}$  for Ni doped Bi<sub>2</sub>Se<sub>3</sub>. Considerable enhancement in the electric field in the vicinity of the thinner and smaller nanoflakes with a low applied voltage causes a favourable field emission. Thus high energy electrons generated due to quantum confinement effect have to cross decreased tunnelling barrier and tunnelling width which allow them to emit at a lower applied bias decreasing the turn-on as well as threshold field. There is also a remarkable increment (about 3 times) in the field enhancement factor when Ni is incorporated in Bi<sub>2</sub>Se<sub>3</sub>. Persistent stability of current was detected for a time span of 3 hours at a constant value of 5 µA. Thus, our results suggest that this Ni doped Bi<sub>2</sub>Se<sub>3</sub> nanostructures can be a pioneering material in the modern technological era of topological insulator field emitters where the degradation of the surface is minimized due to the property of the parent material.

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## **Chapter 6**

## The Conclusion and Future Scope of Research

The core basis of this thesis is to synthesize single crystals as well as nanostructures of bismuth selenide (Bi<sub>2</sub>Se<sub>3</sub>) for their potential application in multifunctional directions. Prominence is given to a modified two-step solid state reaction method known as melt growth method for its exploration in synthesizing Cu intercalated Bi<sub>2</sub>Se<sub>3</sub> single crystals and understanding the fundamentals of their growth processes. Electrical and magnetic properties of these single crystals have been investigated revealing superconducting nature of the sample. Efforts have also been made by adopting two diverse structures of Bi<sub>2</sub>Se<sub>3</sub>, single crystals and nanostructures (synthesized using hydrothermal method), intercalated with copper and doped with nickel respectively to realize highly efficient and stable materials for superconductor, field emission and humidity sensors application.

## **6.1.** Thesis summary

A brief review of topological insulator and one of its material: Bi<sub>2</sub>Se<sub>3</sub> and diverse applications of this material are discussed in *Chapter 1*.

 $Bi_2Se_3$  is one of the few 3D topological insulators to date. It has attracted special attention since Cu intercalation between quintuple layers of  $Bi_2Se_3$  can induce superconductivity below 3.8 K.  $Cu_xBi_2Se_3$  has been proposed to be a leading candidate for topological superconductivity for this reason. Cu-doped  $Bi_2Se_3$  was the first of a series of doped  $Bi_2Se_3$  materials that has been studied in the search for 3D topological superconductivity.

*Chapter 2* describes the main experimental techniques that are employed in this thesis related to the material as well as device fabrication and characterization.

In *Chapter 3* superconducting single crystals of Cu intercalated Bi<sub>2</sub>Se<sub>3</sub> were successfully synthesized through the modified two step melt growth process. The synthesis process was chosen to avoid the formation of Cu<sub>2</sub>Se, since Cu<sub>2</sub>Se is known to inhibit the intercalation of Cu atoms into the van der Waals gap between the Bi<sub>2</sub>Se<sub>3</sub> layers. The XRD results indicate the single crystalline nature of the sample as well as the intercalation of Cu in the layer structure of Bi<sub>2</sub>Se<sub>3</sub>, and this is also confirmed by the Raman data analysis. The  $H_{c2}$  versus  $T_c$  phase diagram obtained with the help of the electrical resistance measurements indicate that in the zero temperature limit the  $H_{c2}$  can be as high as 27.1 kOe when the field is applied parallel to the *c*-axis, though the electrical transport is found to be highly anisotropic in nature. Estimation of the parameters related to the superconducting state, using conventional models, indicate that Cu<sub>0.1</sub>Bi<sub>2</sub>Se<sub>3</sub> is a Pauli limited superconductor. The field dependence of magnetization in the superconducting state seem to be consistent with a spin triplet vortex state with odd parity. In the normal state, on the other hand, the temperature dependence of magnetic susceptibility and the sign of the

magnetoresistance indicate the presence of antiferromagnetic correlations in the sample.

In *Chapter 4* the humidity sensing behaviour of topological insulator single crystals of  $Cu_x Bi_2 Se_3$  (x = 0, 0.13 and 0.25) was reported. The sensitivity of Cu<sub>0.25</sub>Bi<sub>2</sub>Se<sub>3</sub> crystal sensors in response to relative humidity tuned to a value of 849% proves enhancement in sensing behaviour with intercalation of Cu in pure Bi<sub>2</sub>Se<sub>3</sub>. Moreover, other sensing characterizations like low hysteresis and  $T_c$  value (16.78%) with fast response/recovery time of 24s/25s. proposes TIs as ideal material for humidity sensors. The feasible sensing phenomenon is also associated with the Freundlich adsorption model for a conclusive guiding mechanism. The modelled data shows that for  $Cu_{0.25}Bi_2Se_3$  the water adsorption capacity (k) value increases nearly 4 and 2.3 times than that of Bi<sub>2</sub>Se<sub>3</sub> in low and high humidity region, respectively. This confirms increment in number of active sites on surface of TIs which in turn reflected in sensitivity result. Langmuir isotherm model confirms the contribution of adsorption sites over the test period, concluding proportional relationship between sensitivity and humidity. This overall investigation of humidity sensing properties along with theoretical insight thus proposes high possibility and immense potential of Bi<sub>2</sub>Se<sub>3</sub> based TIs for fabrication of multifunctional high performance humidity sensors feasible in near future.

In Chapter 5 the Field Electron Emission property of  $Bi_2Se_3$  and Ni doped  $Bi_2Se_3$  are elaborately described.  $Bi_2Se_3$  and Ni doped  $Bi_2Se_3$  were synthesized by a simple, economical two step synthetic method comprising of chemical bath deposition and hydrothermal synthesis. XRD and SEM results confirm the insertion of Ni ions in  $Bi_2Se_3$  as well as alterations in the thickness and size of the nanostructures of  $Bi_2Se_3$ . Owing to Ni doping, the turn on field of  $Bi_2Se_3$  decreases from 3.2 V  $\mu$ m<sup>-1</sup> to 1.9 V  $\mu$ m<sup>-1</sup> and the threshold field from 4.0 V  $\mu$ m<sup>-1</sup> to 2.5 V  $\mu$ m<sup>-1</sup>. The maximum current density of 173  $\mu$ A cm<sup>-2</sup> is observed at an applied field of 4.4 V  $\mu$ m<sup>-1</sup> for  $Bi_2Se_3$  and 182  $\mu$ A cm<sup>-2</sup> at an applied field of 2.8 V  $\mu$ m<sup>-1</sup> for Ni doped Bi\_2Se\_3.

Considerable enhancement in the electric field in the vicinity of the thinner and smaller nanoflakes with a low applied voltage causes a favourable field emission. Thus high energy electrons generated due to quantum confinement effect have to cross decreased tunnelling barrier and tunnelling width which allow them to emit at a lower applied bias decreasing the turnon as well as threshold field. There is also a remarkable increment (about 3 times) in the field enhancement factor when Ni is incorporated in Bi<sub>2</sub>Se<sub>3</sub>. Persistent stability of current was detected for a time span of 3 hours at a constant value of 5  $\mu$ A. Thus, our results suggest that this Ni doped Bi<sub>2</sub>Se<sub>3</sub> nanostructures can be a pioneering material in the modern technological era of topological insulator field emitters where the degradation of the surface is minimized due to the property of the parent material.

Thus, the verdict of the present study is a decent contribution in the application of topological insulator material Bismuth Selenide. This study also fulfils the main objectives of the thesis and also the thesis title is quite well justified.

## **6.2.** Outlook and Future Prospects

Accounting the benefits from the literature and taking note from different aspects of the present study, the several proposals of future work are in line. A few of them are presented briefly:

First alkali metals (K, Rb and Cs) will be doped in Bi<sub>2</sub>Se<sub>3</sub> single crystals to investigate their superconducting properties followed by measuring the magneto-transport phenomena like resistivity, magnetoresistance, Hall resistance, magnetization, dc susceptibility to construct a theory regarding role of alkali metals in achieving superconductivity in Bi<sub>2</sub>Se<sub>3</sub>.

Second project includes temperature sensing properties of synthesised Ni doped Bi<sub>2</sub>Se<sub>3</sub> nanoparticles to explore a new area on sensing application of topological insulator.

As Bi<sub>2</sub>Se<sub>3</sub> is a TI, unlike other common transition metal oxides it has a unique band structure which can be tuned in various ways by incorporating different transition metals (V, Cr, Sc, Mn, *etc.*) with a systematic study on field emission properties of doped nanomaterials which will include role of individual elements as well as a comparative analysis of the materials resulting in a possible prediction of the best material to maximize the improvement of the property for future industry applications.

For further exploring sensing properties of TIs, we can expand our horizon from humidity sensors to gas sensors which will be able to detect toxic gases like ammonia, carbon dioxide, carbon monoxide, *etc*. The device can be fabricated with not only single crystals but also with the above mentioned nanomaterials of TI. It will open a new door for both sensing and TI scientific communities

As the field of nano devices is nurturing, it becomes increasingly necessary to unravel the underlying working mechanisms of the material/device from both experimental and theoretical aspects. Therefore, there is an immediate need for a deeper understanding of the fundamental mechanisms of the nanostructures before going for direct design.