# UNIVERSIDAD AUTÓNOMA DE NUEVO LEÓN FACULTAD DE INGENIERÍA MECÁNICA Y ELÉCTRICA



### "SOLAR CELLS USING SILVER ANTIMONY SULFOSELENIDE SOLID SOLUTION THIN FILMS AS ABSORBER MATERIAL"

POR

# AISWARYA NADUKKANDY 1988529

# COMO REQUISITO PARCIAL PARA OBTENER EL GRADO DE DOCTOR EN INGENIERIA DE MATERIALES

San Nicolás de los Garza, Nuevo León

Febrero 2023

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### UNIVERSIDAD AUTÓNOMA DE NUEVO LEÓN Facultad de Ingeniería Mecánica y Eléctrica Posgrado

Los miembros del Comité de Evaluación de Tesis recomendamos que la Tesis "Solar cells using silver antimony sulfoselenide solid solution thin films as absorber material", realizada por la estudiante Aiswarya Nadukkandy, con número de matrícula 1988529, sea aceptada para su defensa como requisito parcial para obtener el grado de Doctor en Ingeniería de Materiales.

#### El Comité de Evaluación de Tesis

Dra. Bindu Krishnan Director

Dr. Sadasivan Shaji Revisor

Dr. David Avellaneda Avellaneda Revisor

> Dra. Shadai Lugo Loredo Revisor

Dr. Jorge Oswaldo González Garza Revisor

Dr. Eduardo Martínez Guerra Revisor

Vo.Bo. D Simón Martínez Martínez

Subdirector de Estudios de Posgrado

Institución	190001
Programa	122608

Acta Núm. 318

Ciudad Universitaria, a 27 de marzo de 2023.

# Dedicated to my beloved parents, P Gangadharan and Reetha

For the endless love, support, and encouragement.

### ACKNOWLEDGEMENTS

Huge gratitude to **CONACYT** (Consejo Nacional de Ciencia y Tecnología) for granting research fellowship throughout my Ph.D. programme.

To **CONACYT project** (**CB-2016 -01**, No. <u>**284800**</u>) for the financial assistance during the Ph.D. programme.

To **FIME** (Facultad de Ingeniería Mecánica y Eléctrica) UANL for providing all the experimental and characterization facilities.

To **CIIIA** (Centro de Investigación e Innovación en Ingeniería Aeronáutica) and **CIIDIT** (Centro de Innovación, Investigación y Desarrollo en Ingeniería y Tecnología), UANL for helping with characterization facilities.

I would like to thank my supervisor Dr.Bindu Krishnan for giving me the opportunity to do research and providing invaluable guidance throughout this research. I always value her assistance in improving my experimental and writing skills.

I am grateful to Dr. Sadasivan Shaji for his assistance in making corrections and improving the thesis, as well as for his motivational words throughout the PhD.

I'd also like to thank Dr.David Avellaneda Avellaneda for his guidance, supervision, insightful comments, and empathy throughout my research career.

I am thankful to Dr. Josué Amilcar Aguilar Martínez, Dr. Sanal K.C, Dr. Edgar O. Garcia Sanchez Dra.Maria Isabel Mendivil Palma, Jesus Alejandro Arizpe Zapata and Dra.Selene Sepulveda Guzman, for providing the facility for X-ray diffraction, SEM, EDX and Raman analysis. Also, I express my gratitude towards my seminar evaluators Dr. Domingo García Gutierrez, Dra. Sofia Vázquez Rodríaguez and Dra. Patricia Zambrano Robleado.

I would also like to thank Dr. Azael Martinez de la Cruz and Dr. Simón Martínez Martínez for their supports.

My sincere thanks to Dr. M C Santhosh Kumar for helping me to find a PhD position in Mexico. I am thankful to all my teachers for the constant support throughout my research period.

I am extremely grateful to my whole family members: my grandparents, parents, uncles, aunties, sister, brother, cousins, niece, and nephew etc. for their endless love, care, support,

and blessings and also for letting me to pursue my dream. Thanks to my parents for always supporting me and giving me strength to fulfil my dreams.

A big thanks to all my friends, especially Appu, Anu, Akshana and Albert for their invaluable support, for being there for me whenever I needed a mental support.

I thank my fellow lab mates and friends from Mexico for their help and support throughout my research life. Special thanks to Sreed, Anjali, Dani, Sebin, Katia, Albert, Paulosutty, Pooja, Dra. Claudia, Varshika and Eleazar. I express my gratitude towards Soorya and Ashly. Thanks to all Malayali families, Mexican friends and family for their love.

I would like to thank my beloved Tia Maya, uncle and all other family members for the love, care and support and treating me as one of the family members. I am always grateful to Tia for the endless love and care she gave me throughout my PhD life, considering me as a daughter.

Finally, I am thankful to Almighty for giving me the strength, knowledge, ability, and opportunity to undertake my doctoral study and complete it satisfactorily.

# CONTENTS

Abstractxii
Resumenxiv
List of publicationsxvi
International conferencesxvi
List of Figuresv
List of tablesxiv
Abbreviationsxvi
CHAPTER 11
THIN FILM SOLAR CELLS1
1.1 Thin film solar cells2
1.1.1 Amorphous silicon4
1.1.2 Cadmium telluride5
1.1.3 Copper indium selenide (CIS) and copper indium gallium selenide (CIGS)
5
1.2 Emerging thin film solar cells6
1.2.1 Dye-Sensitized solar cells (DSSC)6
1.2.2 Organic and polymer solar cells7
1.2.3 Perovskite solar cells7
1.2.4 Copper Zinc Tin Sulfide (CZTS)7
1.2.5 Antimony sulfide (Sb2S3) and antimony sulfoselenide (Sb2(S1-xSex)3
1.2.6 Copper antimony sulfide (CuSbS <sub>2</sub> )8
1.2.7 Silver antimony sulfide, selenide and sulfoselenide9
1.3 Hypothesis

1.4 Objectives 10
1.4.1 General objective10
1.4.2 Specific objectives11
1.5 Justification11
CHAPTER 2
THEORETICAL STUDIES13
2.1 VASP
2.1.1 Crystal structure14
2.1.2 Band structure and density of states17
2.2 SOLAR CELL CAPACITANCE SIMULATOR-1 DIMENSIONAL (SCAPS-1D)
2.2.1 AgSbS2-xSex solar cells
CHAPTER 3
EXPERIMENTAL DETAILS: SILVER ANTIMONY SULFIDES AND
SULFOSELENIDES
SULFOSELENIDES       24         3.1 Thin film deposition techniques       24         3.1.1 Chemical bath deposition (CBD)       24         3.1.2 Thermal evaporation technique       25         3.1.3 Spin coating       26         3.1.4 Pulsed laser irradiation in liquid       27
SULFOSELENIDES.       24         3.1 Thin film deposition techniques       24         3.1.1 Chemical bath deposition (CBD)       24         3.1.2 Thermal evaporation technique       25         3.1.3 Spin coating       26         3.1.4 Pulsed laser irradiation in liquid       27         3.2 Silver antimony sulfide (AgSbS2)       28
SULFOSELENIDES       24         3.1 Thin film deposition techniques       24         3.1.1 Chemical bath deposition (CBD)       24         3.1.2 Thermal evaporation technique       25         3.1.3 Spin coating       26         3.1.4 Pulsed laser irradiation in liquid       27         3.2 Silver antimony sulfide (AgSbS2)       28         3.3 Silver antimony sulfoselenide synthesis (AgSbS2-xSex)       29
SULFOSELENIDES
SULFOSELENIDES       24         3.1 Thin film deposition techniques       24         3.1.1 Chemical bath deposition (CBD)       24         3.1.2 Thermal evaporation technique       25         3.1.3 Spin coating       26         3.1.4 Pulsed laser irradiation in liquid       27         3.2 Silver antimony sulfide (AgSbS2)       28         3.3 Silver antimony sulfoselenide synthesis (AgSbS2-xSex)       29         3.4 Synthesis of Se and Se:Graphene nanocolloid       29         3.5 Preparation of AgSbS2-xSex and AgSbS2-xSex:Graphene thin films       30
SULFOSELENIDES.       24         3.1 Thin film deposition techniques       24         3.1.1 Chemical bath deposition (CBD).       24         3.1.2 Thermal evaporation technique       25         3.1.3 Spin coating       26         3.1.4 Pulsed laser irradiation in liquid.       27         3.2 Silver antimony sulfide (AgSbS2).       28         3.3 Silver antimony sulfoselenide synthesis (AgSbS2-xSex)       29         3.4 Synthesis of Se and Se:Graphene nanocolloid       29         3.5 Preparation of AgSbS2-xSex and AgSbS2-xSex:Graphene thin films.       30         3.6 Device fabrication: solar cells and photodetectors       30
SULFOSELENIDES       24         3.1 Thin film deposition techniques       24         3.1.1 Chemical bath deposition (CBD)       24         3.1.2 Thermal evaporation technique       25         3.1.3 Spin coating       26         3.1.4 Pulsed laser irradiation in liquid       27         3.2 Silver antimony sulfide (AgSbS2)       28         3.3 Silver antimony sulfoselenide synthesis (AgSbS2-xSex)       29         3.4 Synthesis of Se and Se:Graphene nanocolloid       29         3.5 Preparation of AgSbS2-xSex and AgSbS2-xSex:Graphene thin films       30         3.6 Device fabrication: solar cells and photodetectors       30         3.6.1 Solar cells: glass/FTO/CdS/AgSbS2/C/Ag and glass/FTO/CdS/AgSbS2-       28

3.6.2 Photodetectors	31
3.7 Characterization	32
3.7.1 X-ray diffraction (XRD)	32
3.7.2 Raman spectroscopy	32
3.7.3 X-ray Photoelectron spectroscopy (XPS)	32
3.7.4 Scanning electron microscopy (SEM) and energy dispersive X-ray	
spectroscopy	33
(EDX)	33
3.7.5 Transmission electron microscopy (TEM)	34
3.7.6 Atomic force microscopy (AFM)	34
3.7.7 UV-Vis-NIR spectroscopy	34
3.7.8 Electrical characterization	35
3.7.9 J-V measurements	35
CHAPTER 4	40
CHAPTER 4	40 40
CHAPTER 4	40 40 40
CHAPTER 4	40 40 40 40
CHAPTER 4	40 40 40 40
CHAPTER 4	40 40 40 40 45 49
CHAPTER 4AgSbS2 THIN FILMS FOR PHOTOVOLTAIC APPLICATIONSA 4.2 Results and discussionsA 4.2.1 StructureA 4.2.2 CompositionA 4.2.3 MorphologyA 4.2.4 Optical propertiesA	40 40 40 40 45 49 53
CHAPTER 4	<ul> <li>40</li> <li>40</li> <li>40</li> <li>40</li> <li>45</li> <li>49</li> <li>53</li> <li>55</li> </ul>
CHAPTER 4	40 40 40 45 49 53 55 57
CHAPTER 4	<ul> <li>40</li> <li>40</li> <li>40</li> <li>40</li> <li>45</li> <li>49</li> <li>53</li> <li>55</li> <li>57</li> <li>59</li> </ul>
CHAPTER 4 AgSbS2 THIN FILMS FOR PHOTOVOLTAIC APPLICATIONS	40 40 40 45 49 53 55 57 59
CHAPTER 4 AgSbS2 THIN FILMS FOR PHOTOVOLTAIC APPLICATIONS	<ul> <li>40</li> <li>40</li> <li>40</li> <li>40</li> <li>45</li> <li>49</li> <li>53</li> <li>55</li> <li>57</li> <li>59</li> <li>59</li> </ul>

5.1.1 Crystal structure: Effect of Ag thickness and selenization time 59
5.1.2 Elemental composition and chemical state
5.1.3 Morphology
5.1.5 Electrical studies
5.1.6 Photodetectors
5.1.7 Photovoltaic device96
CHAPTER 6
AgSbS2-xSex AND GRAPHENE INCORPORATED AgSbS2-xSex FILMS USING
Se:GRAPHENE NANOCOLLOIDS FOR OPTOELECTRONICS104
6.1 Results and discussions104
6.1.1 Characterization of Se, Se:Gr nanocolloid104
6.1.2 Crystal structure and solid solution stoichiometry
6.1.3 Optical properties110
6.1.4 Morphology113
6.1.5 Electrical properties113
6.1.5 Electrical properties113 6.1.6 Crystal structure: effect of heating temperature on AgSbS2-xSex thin films
6.1.5 Electrical properties
6.1.5 Electrical properties
6.1.5 Electrical properties       113         6.1.6 Crystal structure: effect of heating temperature on AgSbS2-xSex thin films       115         6.1.7 Chemical composition       116         6.1.8 Morphological studies       118
6.1.5 Electrical properties       113         6.1.6 Crystal structure: effect of heating temperature on AgSbS2-xSex thin films       115         6.1.7 Chemical composition       116         6.1.8 Morphological studies       118         6.1.9 Effect of heating conditions on optical properties       119
6.1.5 Electrical properties       113         6.1.6 Crystal structure: effect of heating temperature on AgSbS2-xSex thin films       115
6.1.5 Electrical properties       113         6.1.6 Crystal structure: effect of heating temperature on AgSbS2-xSex thin films       115
6.1.5 Electrical properties       113         6.1.6 Crystal structure: effect of heating temperature on AgSbS2-xSex thin films       115         6.1.7 Chemical composition       116         6.1.8 Morphological studies       118         6.1.9 Effect of heating conditions on optical properties       119         6.1.10 Electrical properties       121         6.1.11 Photovoltaic device       121         6.1.12 Photodetector       122
6.1.5 Electrical properties       113         6.1.6 Crystal structure: effect of heating temperature on AgSbS2-xSex thin films       115         6.1.6 Crystal structure: effect of heating temperature on AgSbS2-xSex thin films       115         6.1.7 Chemical composition       116         6.1.8 Morphological studies       118         6.1.9 Effect of heating conditions on optical properties       119         6.1.10 Electrical properties       121         6.1.11 Photovoltaic device       121         6.1.12 Photodetector       122         6.1.13 Graphene incorporated AgSbS2-xSex thin films       133
6.1.5 Electrical properties1136.1.6 Crystal structure: effect of heating temperature on AgSbS2-xSex thin films1156.1.7 Chemical composition1166.1.8 Morphological studies1186.1.9 Effect of heating conditions on optical properties1196.1.10 Electrical properties1216.1.11 Photovoltaic device1216.1.12 Photodetector1226.1.13 Graphene incorporated AgSbS2-xSex thin films1336.1.14 Chemical state135

6.1.16 Optical properties of AgSbS2-xSex:Graphene thin films	
6.1.17 Studies on electrical properties of AgSbS <sub>2-x</sub> Se <sub>x</sub> :Graphe	ne thin films 139
6.1.18 Photovoltaic device	140
6.1.19 Self-powered photodetectors	
CHAPTER 7	145
GENERAL CONCLUSIONS AND OUTLOOK	145
SCOPE OF THE WORK	147
References	

### ABSTRACT

Thin film solar cells have got greater importance than conventional Si wafer based solar cells mainly due to low cost of production and use of the flexible substrate. During the past few decades, continuous work has been going on to produce novel materials. CdTe and CIGS are the most widely used chalcopyrites in solar cells. These materials have acquired comparable efficiency with Si solar cells. However, the issues of toxicity and scarcity of the constituent elements are remained to be solved for their large-scale application. World-wide efforts are in advance to explore new multinary chalcogenides. Copper zinc tin sulfide (CZTS) is one such promising material due to the presence of less toxic, low cost and earth-abundant constituent elements. Materials of sulfides/selenides with low-cost raw materials and lowcost production processes are projected for innovative PV technology. Silver antimony sulfide (AgSbS<sub>2</sub>) and silver antimony sulfoselenides (AgSbS<sub>2-x</sub>Se<sub>x</sub>) are novel chalcogenides with suitable optoelectronic properties for solar cell applications. Special attention has been given to the study of structure, morphology, composition and opto-electronic properties of AgSbS<sub>2</sub> thin films and their incorporation in photovoltaic structures. The best solar cell with  $AgSbS_2$  absorber and CdS window layer resulted in an efficiency of 1.5 %. In addition, we also focused on theoretical investigation of these materials using First Principle calculation based on density functional theory (DFT). It includes crystal structure, electronic band structure and density of state studies of monoclinic AgSbS<sub>2</sub>. The main objective of this thesis is to synthesize and fabricate silver antimony sulfoselenides thin films and photovoltaic devices. AgSbS<sub>2-x</sub>Se<sub>x</sub> is a quaternary metal chalcogenide with tunable optical bandgap (1.1-1.8 eV). We studied the structural, morphological, optical and electrical properties of the AgSbS<sub>2-x</sub>Se<sub>x</sub> thin films with different x values formed by varying Se/S and Ag/Sb ratio in detail. The champion cell with structure Glass/FTO/n-CdS/p-AgSbS<sub>2-x</sub>Se<sub>x</sub>/C/Ag yielded Voc = 525 mV,  $J_{sc} = 15 \text{ mA/cm}^2$ , FF = 0.53 with an ever-reported conversion efficiency of 4.2%. We also explored the photodetector application of these materials for the first time. The developed device showed high sensitivity and stability in the wide range of wavelengths (UV-Vis-NIR). Furthermore, AgSbS<sub>2-x</sub>Se<sub>x</sub> thin films were also prepared using Se nanocolloid synthesized by laser irradiation method and incorporated graphene into the films to improve the electrical properties. Self-powered photodiodes were developed with these materials with high detection sensitivity in UV-Vis-NIR region. Further, SCAPS-1D simulation studies of CdS/AgSbS<sub>2-x</sub>Se<sub>x</sub> photovoltaic device is also presented. The synthesis, characterization and device applications explained in different chapters of the thesis can provide a complete knowledge of AgSbS<sub>2</sub> and AgSbS<sub>2-x</sub>Se<sub>x</sub> and this work can inspire to do more research on these materials for photovoltaic and other opto-electronic applications.

### RESUMEN

Las celdas solares de película delgada han logrado tener una mayor importancia que las celdas convencionales basadas en silicio, principalmente debido al bajo costo de producción y al uso de sustratos flexibles. Durante las últimas décadas, se ha trabajado continuamente para producir materiales novedosos, tales como el teluro de cadmio (CdTe) y el cobre-indio-galio-selenio (CIGS), que son los calcogenuros más utilizados actualmente en las celdas solares. Estos materiales han adquirido una eficiencia comparable a la de celdas basadas en silicio. Sin embargo, aún quedan por resolver los problemas de toxicidad y escasez de los elementos constituyentes para su aplicación a gran escala. Se están realizando esfuerzos a nivel mundial para explorar nuevos calcogenuros multinarios. El sulfuro de cobre, zinc y estaño (CZTS) es uno de esos materiales prometedores debido a la presencia de elementos constituyentes menos tóxicos, de bajo costo y abundantes en la corteza terrestre. Se proyectan materiales de sulfuros/seleniuros con materias primas y procesos de producción de bajo costo para una tecnología fotovoltaica innovadora.

El sulfuro de plata antimonio (AgSbS<sub>2</sub>) y los sulfoselenuros de plata antimonio (AgSbS<sub>2</sub>-<sub>x</sub>Se<sub>x</sub>) son nuevos calcogenuros con propiedades optoelectrónicas adecuadas para aplicaciones de celdas solares. Se ha prestado especial atención al estudio de la estructura, morfología, composición y propiedades optoelectrónicas de películas delgadas de AgSbS2 y su incorporación en estructuras fotovoltaicas. La mejor celda solar empleando como material absorbedor el AgSbS<sub>2</sub> y como capa ventana al CdS, dio como resultado una eficiencia de conversión del 1,5 %. Además, también nos enfocamos en la investigación teórica de estos materiales utilizando cálculos basados en la teoría funcional de la densidad (DFT). Se incluyen estudios de la estructura cristalina, estructura de bandas y densidad de estados de las películas de AgSbS<sub>2</sub> monoclínicas. El objetivo principal de esta tesis es sintetizar y fabricar películas delgadas de sulfoselenuros de plata y antimonio, además de dispositivos fotovoltaicos. El AgSbS<sub>2-x</sub>Se<sub>x</sub> es un calcogenuro de metal cuaternario con banda prohibida óptica ajustable (1,1-1,8 eV). Estudiamos en detalle las propiedades estructurales, morfológicas, ópticas y eléctricas de las películas delgadas de  $AgSbS_{2-x}Se_x$  con diferentes valores de x formados por la variación de la relación Se/S y Ag/Sb. La celda con mejores resultados tiene una estructura: vidrio/FTO/n-CdS/p-AgSbS<sub>2-x</sub>Se<sub>x</sub>/C/Ag, y mostró un voltaje de circuito abierto, V<sub>oc</sub> = 525 mV, densidad de corriente de corto circuito, J<sub>sc</sub> = 15 mA/cm<sup>2</sup>, factor de forma, FF = 0,53 y una eficiencia de conversión del 4.2 %. También exploramos la aplicación de estos materiales como fotodetectores por primera vez. El dispositivo desarrollado mostró alta sensibilidad y estabilidad en el amplio rango de longitudes de onda (UV-Vis-NIR). Además, también se prepararon películas delgadas de AgSbS<sub>2-x</sub>Se<sub>x</sub> utilizando nanocoloides de Se sintetizado mediante el método de irradiación láser y se incorporó grafeno en las películas, para mejorar sus propiedades eléctricas. Con estos materiales se desarrollaron fotodiodos autoalimentados con alta sensibilidad de detección en la región UV-Vis-NIR. Se presentan también, los estudios de simulación SCAPS-1D del dispositivo fotovoltaico basado en CdS/AgSbS<sub>2-x</sub>Se<sub>x</sub>. Las aplicaciones de la síntesis, caracterización y la incorporación en dispositivos que es explicado en diferentes capítulos de esta tesis, pueden proporcionar un conocimiento completo sobre los materiales de AgSbS<sub>2</sub> y AgSbS<sub>2-x</sub>Se<sub>x</sub>, pudiendo este trabajo lograr mayor inspiración a investigar más sobre estos materiales.

# LIST OF PUBLICATIONS INTERNATIONAL JOURNALS

- A. Nadukkandy, S. Shaji, D.A. Avellaneda, J.A. Aguilar-martínez, B. Krishnan, Cubic structured silver antimony sulfide-selenide solid solution thin films for sustainable photodetection and photovoltaic application, J. Alloys Compd. 942 (2023) 169072. https://doi.org/10.1016/j.jallcom.2023.169072.
- A. Parameswaran Sreekala, A. Nadukkandy, S. Shaji, D.A. Avellaneda, J.A. Aguilar-Martínez, B. Krishnan, AgSbS<sub>2-x</sub>Se<sub>x</sub> thin films: Structure, composition, morphology and photodetection properties, Mater. Today Commun. 27 (2021) 102362. <u>https://doi.org/10.1016/j.mtcomm.2021.102362</u>.
- A. Nadukkandy, S. Devasia, Bindu Kirishnan, P. Abraham, S. Shaji, D. Avellaneda, J.A. Aguilar-martínez, E. Gandara, Monoclinic AgSbS<sub>2</sub> thin films for photovoltaic applications: Computation, growth and characterization approaches, Mater. Sci. Semicond. Process. 135 (2021) 106074.

https://doi.org/10.1016/j.mssp.2021.106074.

### **INTERNATIONAL CONFERENCES**

- Oral presentation in Photovoltaics, Solar Energy Materials and Technologies Symposium at the XXIX International Materials Research Congress 2021, from August 15<sup>th</sup> to 20<sup>th</sup>, held at Cancun, Mexico.
- Oral presentation at XV International Conference on Surfaces, Materials and Vacuum 2022, September 20<sup>th</sup>, Puerto Vallarta, Jalisco, Mexico.
- Poster presentation at European Materials Research Society (E-MRS) Spring meeting 2022, May 30<sup>th</sup> to June 3<sup>rd</sup>, Virtual conference.
- Oral presentation in International Webinar Series, Progress and Promises in Chemical Sciences (PPCS 2021), March 22<sup>nd</sup> to 28<sup>th</sup>, CHRIST, Bengaluru, India.

# **List of Figures**

Figure 1.1 Efficiency and cost comparison of different photovoltaic technologies [10] 2
Figure 1.2 a) Schematic illustration of thin film solar cells b) J-V characteristics of solar
cell under dark and illumination [14] c) circuit diagram of solar cell
Figure 1.3 Certified efficiencies of different solar cells, NREL
https://www.nrel.gov/pv/cell-efficiency.html (accessed January 4 2020)
Figure 2.1 Calculation flow chart of VASP
Figure 2.2 a) Unit cell of monoclinic $AgSbS_{2}$ . Reproduced with kind permission from
Elsevier [110] b) (400) c) (312) d) (115) planes along c axis [111]
Figure 2.3 a) $2 \times 2 \times 2$ supercell of AgSbS <sub>2</sub> /Se <sub>2</sub> b) (111) c) (200) and d) (220) planes along c
axis16
Figure 2.4 $AgSbS_2$ a) electronic band structure (b) total and partial density of states.
Reproduced with kind permission from Elsevier [110]17
Figure 2.5 a) Electronic band structure of $AgSbS_2$ b) Total and partial density of states
$AgSbS_2$ c) Electronic band structure $AgSbSe_2$ d) Total and partial density of states $AgSbSe_2$ .
Figure 2.6 Solar cell structure
Figure 2.7 Simulated J-V characteristics using SCAPS (a) $CdS/AgSbS_{1.28}Se_{0.72}$ single
junction solar cells with varying absorber layer thickness and a fixed bandgap of 1.55 eV b)
$CdS/AgSbS_{2-x}Se_x$ with varying bandgap for a fixed thickness of 400 nm c) highest possible
efficiency using bandgap 1.2 eV and maximum thickness of 1000 nm

Figure 3.1 Photographs of chemical bath deposition technique before and after deposition.

	. 24
Figure 3.2 Photograph of thermal evaporator (Torr international)	. 25
Figure 3.3 Photograph of compact spin coater system and thin film.	. 27
Figure 3.4 Photograph of pulsed laser irradiation in liquid using ND:YAG laser	. 28
Figure 3.5 Schematic representation of preparation of AgSbS <sub>2</sub> thin films.	. 29

Figure 4.1 Photographs of Sb <sub>2</sub> S <sub>3</sub> , Sb <sub>2</sub> S <sub>3</sub> -Ag and AgSbS <sub>2</sub> thin films on glass40
Figure 4.2 a) XRD of as prepared and heated $Sb_2S_3$ and heated $Sb_2S_3$ -Ag thin films with
varying silver thickness (Ag = 5, 10, and 20 nm), b) $Sb_2S_3/Ag$ , with silver thickness as 50,
60, 80, 100, and 110 nm (a) as prepared (b) thin films heated at 350 $^{\circ}$ C, 30 minutes in vacuum.
Reproduced with kind permission from Elsevier [108]42
Figure 4.3 W-H plot of AgSbS50, AgSbS60, AgSbS80, AgSbS100 and AgSbS110 thin films.
Reproduced with kind permission from Elsevier [108]44
Figure 4.4 High resolution TEM image of AgSbS50 sample. Reproduced with kind
permission from Elsevier [108]45
Figure 4.5 XPS survey spectrum of AgSbS100 sample46
Figure 4.6 XPS high resolution core level spectra of (a) Ag3d, (b) Sb3d, and (c) S2p of
glass/Sb <sub>2</sub> S <sub>3</sub> -Ag precursor layer. Reproduced with kind permission from Elsevier [108]47
Figure 4.7 XPS high resolution spectra of the core levels of (a) Ag 3d, (b) Sb 3d, and (c)S 2p
of AgSbS100. Reproduced with kind permission from Elsevier [108]48
Figure 4.8 Depth profile analysis of a) glass/Sb <sub>2</sub> S <sub>3</sub> -Ag b) AgSbS100. Reproduced with kind
permission from Elsevier [108]49
Figure 4.9 Scanning electron micrographs of AgSbS <sub>2</sub> thin films (a) AgSbS50 (c)
AgSbSbS100 (e) AgSbS110 as deposited and (b) AgSbS50 (d) AgSbS100 (f) AgSbS110 (g)
AgSbS60 (h) AgSbS80 annealed at 350 °C for 30 minutes in vacuum. Reproduced with kind
permission from Elsevier [108]50
Figure 4.10 Atomic force micrographs of (2D) (a) AgSbS50, (c) AgSbS100, (d) AgSbS110
and (b, e, and f) their corresponding 3D images. Reproduced with kind permission from
Elsevier [108]
Figure 4.11 Contact error images of (a) AgSbS50, (b) AgSbS100 and (c) AgSbS110 samples.
Reproduced with kind permission from Elsevier [108]52
Figure 4.12 EDX mapping of AgSbS50 sample53

Figure 4.13 a) Absorbance spectra b) transmittance and reflectance spectra c) Tauc plots of
AgSbS50, AgSbS60, AgSbS80, AgSbS100 and AgSbS110 thin films. Reproduced with kind
permission from Elsevier [108]54
Figure 4.14 Photoresponse curve of heated $Sb_2S_3/Ag$ films with silver thickness a) 10 nm b)
20 nm and c) 50 nm, cyclic photoresponse of d)10, 20, and 50nm. Reproduced with kind
permission from Elsevier [108]56
Figure 4.15 Schematic of glass/FTO/n-CdS/p-AgSbS <sub>2</sub> /C/Ag solar cell
Figure 4.16 J-V characteristics of (a) glass/FTO/n-CdS/p-AgSbS <sub>2</sub> /carbon/silver structure in
which Ag thickness is a) 10, 20 and 50 nm b) 60 and 80 nm. Reproduced with kind permission
from Elsevier [108]58

Figure 5.1 Photographs of precursor layers and AgSbS <sub>2-x</sub> Se <sub>x</sub> thin films
Figure 5.2 a) XRD patterns of heated glass/Sb <sub>2</sub> S <sub>3-</sub> Ag <sub>2</sub> Se films with silver thickness 10, 20,
40, 60 and 80 nm b) normalized (200) peak. Reproduced with kind permission from Elsevier
[109]60
Figure 5.3 XRD patterns of (a) selenized glass/Sb <sub>2</sub> S <sub>3</sub> -Ag thin film(b) post-annealed for $350^{\circ}$ C
for 30 minutes in vacuum with Ag thickness 50, 100 and 100 nm (50AgSbSSe, 100AgSbSSe,
110AgSbSSe). Also, zoomed image of (200) peaks in the inset). The standard patterns of
cubic AgSbS <sub>2</sub> and AgSbSe <sub>2</sub> are also included62
Figure 5.4 Williamson- Hall plot of 50AgSbSSe, 100AgSbSSe and 110AgSbSSe thin films.
Figure 5.5 XRD patterns of heated glass/Sb <sub>2</sub> S <sub>3</sub> -Ag <sub>2</sub> Se films with a) 100 nm Ag layer and dip
selenization for1, 5-, 15- and 20-minutes b) 50 nm Ag thickness dip selenization for 1, 5, 15,
20 and 30 minutes, normalized (200) peak is present in the inset
Figure 5.6 Williamson- Hall plot of 50AgSbSSe15, 50AgSbSSe20 and 50AgSbSSe30 thin
films
Figure 5.7 High resolution XPS spectra of (a) Ag 3d, (b) Sb 3d, (c) S 2p, (d) Se 3d of
glass/Sb <sub>2</sub> S <sub>3</sub> -Ag <sub>2</sub> Se thin film after one cycle of etching67
Figure 5.8 XPS a) survey spectra and core level spectra of (b) Ag 3d, (c) Sb 3d, (d) S 2p, (e)
Se 3d of 100AgSbSSe after one cycle of etching68

Figure 5.9 XPS core level spectra of (a) Ag 3d, (b) Sb 3d, (c) S 2p, (d) Se 3d of 50AgSbSSe. Figure 5.10 XPS depth profile and depth profile for composition of the film for Ag 3d, Sb 3d, Se 3d and S 2p in Ag<sub>2</sub>Se-Sb<sub>2</sub>S<sub>3</sub> a) and b), 100AgSbSSe thin films c) and (d) respectively. Figure 5.11 XPS core level spectra of 40(a-d) and 80 nm (e-h) AgSbS<sub>2-x</sub>Se<sub>x</sub> films. Reproduced with kind permission from Elsevier [109].....72 Figure 5.12 XPS spectra of the core levels of (a) Ag 3d, (b) Sb 3d, (c) S 2p, (d) Se 3d of 50AgSbSSe15......73 Figure 5.13 XPS spectra of the core levels of (a) Ag 3d, (b) Sb 3d, (c) S 2p, (d) Se 3d of 50AgSbSSe20......73 Figure 5.14 XPS spectra of the core levels of (a) Ag 3d, (b) Sb 3d, (c) S 2p, (d) Se 3d of 50AgSbSSe30......74 Figure 5.15 EDX mapping of a)50AgSbSSe b)100AgSbSSe c)110AgSbSSe d)50AgSbSSe15 e) 50AgSbSSe20 and f) 50AgSbSe30......78 Figure 5.16 Scanning electron micrographs of Ag<sub>2</sub>Se-Sb<sub>2</sub>S<sub>3</sub> precursor layers with varying silver thickness and the respective AgSbS<sub>2-x</sub>Se<sub>x</sub> films formed a) Ag<sub>2</sub>Se-Sb<sub>2</sub>S<sub>3</sub> with Ag 50 nm b) 50AgSbSSe (AgSbS<sub>1,42</sub>Se<sub>0.58</sub>) c) Ag<sub>2</sub>Se-Sb<sub>2</sub>S<sub>3</sub> with Ag 100nm d) 100AgSbSSe (AgSbS<sub>1.38</sub>Se<sub>0.62</sub>) e) Ag<sub>2</sub>Se-Sb<sub>2</sub>S<sub>3</sub> with Ag 110 nm and f) 110AgSbSSe (AgSbS<sub>1.36</sub>Se<sub>0.64</sub>). 80 Figure 5.17 SEM images of AgSbS<sub>2-x</sub>Se<sub>x</sub> films with Ag 50 nm selenized for different time a) Ag<sub>2</sub>Se-Sb<sub>2</sub>S<sub>3</sub> (15 min) b) 50AgSbSSe15 (AgSbS<sub>1.28</sub>Se<sub>0.72</sub>) c) Ag<sub>2</sub>Se-Sb<sub>2</sub>S<sub>3</sub> (20 min) d) 50AgSbSSe20(AgSbS<sub>1.24</sub>Se<sub>0.78</sub>) e) Ag<sub>2</sub>Se-Sb<sub>2</sub>S<sub>3</sub> (20 min) f) 50AgSbSSe30 (AgSbS<sub>1.16</sub>Se<sub>0.84</sub>). Figure 5.18 SEM images of SEM images of a) 10 nm, b) 40 nm, c) 60 nm and d) 80 nm films. Figure 5.19 SEM cross section of glass/Sb<sub>2</sub>S<sub>3</sub>-Ag<sub>2</sub>Se and AgSbS<sub>2-x</sub>Se<sub>x</sub>/glass layers.........82 Figure 5.20 Reflectance and transmittance spectra of I, a)50AgSbSSe b)100AgSbSSe c)110AgSbSSe and II a) 50AgSbSSe15 b) 50AgSbSSe20 c) 50AgSbSSe30......83 Figure 5.21 Absorption spectra of 50AgSbSSe, 100AgSbSSe and 110AgSbSSe films, the 

Figure 5.22 Absorption spectra of 50AgSbSSe15, 50AgSbSSe20 and 50AgSbSSe30 films,
the respective Tauc plots and bandgap values are given in inset
Figure 5.23 T and R spectra of films with Ag - 40, 60 and 80 nm
Figure 5.24 Optical absorption spectra of $AgSbS_{2-x}Se_x$ films, Tauc plot is given in the inset.
Reproduced with kind permission from Elsevier [109]86
Figure 5.25 Photocurrent response curves of $AgSbS_{2-x}Se_x$ thin films with different $Ag$
thickness $50AgSbSSe(AgSbS_{1.42}Se_{0.58})$ , $100AgSbSSe(AgSbS_{1.38}Se_{0.62})$ , $110AgSbSSe$
(AgSbS1.36Se0.64) and varying selenization time 50AgSbSSe15(AgSbS1.28Se0.72)
50AgSbSSe20(AgSbS <sub>1.24</sub> Se <sub>0.78</sub> ) and 50AgSbSSe30(AgSbS <sub>1.16</sub> Se <sub>0.84</sub> )
Figure 5.26 Photoresponse curves of $AgSbS_{2-x}Se_x$ with $Ag = 100$ nm and varying selenization
time a) 100AgSbSSe15 (AgSbS <sub>1.36</sub> Se <sub>0.64</sub> and b) 100AgSbSSe20 (AgSbS <sub>1.35</sub> Se <sub>0.65</sub> )88
Figure 5.27 Schematic of AgSbS <sub>2-x</sub> Se <sub>x</sub> photodetector
Figure 5.28 (a) Photoresponse of the samples using 465 nm, 520 nm, 590 nm and 620 nm
LEDs (b) cyclic photoresponse of the same samples. Reproduced with kind permission from
Elsevier [109]
Figure 5.29 Sensitivity vs wavelength plot for different samples. Reproduced with kind
permission from Elsevier [109]91
Figure 5.30 Photoresponse to various laser powers ranging from 8 mW-24 mW and bias
voltage of 0.5 V. Reproduced with kind permission from Elsevier [109]92
Figure 5.31 Photoresponse to lasers with power densities ranging from 6.06 - 45.45 $mW/cm^2$
(applied voltage 0.5 V). Reproduced with kind permission from Elsevier [109]92
Figure 5.32 Plot of a) responsivity vs power density b) sensitivity vs power density, with
varying power. Reproduced with kind permission from Elsevier [109]
Figure 5.33 The on-off behavior of $AgSbS_{2-x}Se_x$ photodetector to UV an IR LEDs.
Reproduced with kind permission from Elsevier [109]95
Figure 5.34 a) Schematic representation of glass/FTO/n-CdS/p-AgSbS <sub>2-x</sub> Se <sub>x</sub> /C/Ag solar cell,
b) cross section SEM image of a complete solar cell prior to electrode coating, J-V
characteristics of solar cells c) using $AgSbS_{2-x}Se_x$ with different compositions d)
100AgSbSSe15 and 100AgSbSSe2097
Figure 5.35 J-V characteristics of solar cells with a) 50-50AgSbSSe,50-100AgSbSSe and b)
80AgSbSSe10-10 and 50AgSbSSe10-10 absorber layers

Figure 5.36 External quantum efficiency spectrum (EQE) of device with	AgSbS <sub>2-x</sub> Se <sub>x</sub>
absorber layer with silver thickness 100 nm.	
Figure 5.37 Cyclic photoresponse of $AgSbS_{1.28}Se_{0.72}$ photodiode under zero	bias with a)
halogen lamp, b) LEDs and c) 1064 nm laser.	

Figure 6.1 Se powder dissolved in DW, acetone and IPA and Se nanocolloid formed after
laser irradiation104
Figure 6.2 Schematic of Se:Graphene nanocolloid
Figure 6.3 XRD pattern of bulk selenium powder
Figure 6.4 SEM images of a) bulk Se powder, Se nanoparticles after irradiation in different
solvents such as b) distilled water c) acetone c) IPA, e) Se:Graphene nanoparticles in IPA.
Figure 6.5 TEM images of Se nanoparticles by laser irradiation in a) DW b) acetone c) IPA
and d) EDX
Figure 6.6 XRD patterns of as prepared Se-Ag-Sb <sub>2</sub> S <sub>3</sub> /glass precursor
Figure 6.7 XRD patterns of AgSbS <sub>2-x</sub> Se <sub>x</sub> thin films using Se nanocolloids in different solvents
a) single deposition (20 ml nanocolloid), b) multi deposition (40 ml) c) normalized peak
intensity image of (200) peak
Figure 6.8 a) absorption b) transmittance and reflectance e) Tauc plot of AgSbS <sub>2-x</sub> Se <sub>x</sub> films
prepared by single deposition (20 ml) of Se nanocolloid in DW, acetone and IPA, c)
absorption d) transmittance and reflectance f) Tauc plot of AgSbS <sub>2-x</sub> Se <sub>x</sub> films by multi-
deposition (40 ml) of Se nanocolloid in acetone and IPA
Figure 6. 9 SEM images of AgSbS <sub>2-x</sub> Se <sub>x</sub> films with different stoichiometry a) AgSbS <sub>0.94</sub> Se <sub>1.06</sub> ,
b) AgSbS <sub>0.90</sub> Se <sub>1.10</sub> , c) AgSbS <sub>0.88</sub> Se <sub>1.12</sub> , d) AgSbS <sub>0.62</sub> Se <sub>1.38</sub> and e) AgSbS <sub>0.60</sub> Se <sub>1.40</sub>
Figure 6.10 Photocurrent response of AgSbS <sub>2-x</sub> Se <sub>x</sub> films with single (20 ml) and multi-
deposition (40 ml) of Se nanocolloid in different solvents
Figure 6.11 XRD patterns of Se-Ag-Sb <sub>2</sub> S <sub>3</sub> /glass a) as prepared b) heated at 325 °C, 350 °C
and 375 °C. The normalized (intensity) (200) peak is given in the inset
Figure 6.12 XPS a) survey spectra, high resolution spectra of b) Ag 3d c) Sb 3d d) S 2p e) Se
3d in AgSbS <sub>0.66</sub> Se <sub>1.34</sub>

Figure 6.13 XPS depth profile for Ag 3d, Sb 3d, Se 3d and S 2p in a) as prepared and b)
AgSbS <sub>0.66</sub> Se <sub>1.34</sub> thin films
Figure 6.14 SEM images of AgSbS <sub>2-x</sub> Se <sub>x</sub> films heated at a) 325 °C (AgSbS <sub>0.84</sub> Se <sub>1.16</sub> ) b) 350
°C (AgSbS <sub>0.66</sub> Se <sub>1.34</sub> ) and c) 375 °C (AgSbS <sub>0.70</sub> Se <sub>1.30</sub> )
Figure 6.15 Reflectance and transmittance spectra b) absorption spectra and c) absorption
coefficient vs energy, Tauc plot is given in the inset
Figure 6.16 Photoresponse curve for AgSbS <sub>0.84</sub> Se <sub>1.16</sub> , AgSbS <sub>0.66</sub> Se <sub>1.34</sub> and AgSbS <sub>0.70</sub> Se <sub>1.30</sub>
films heated at 325 °C, 350 °C and 375 °C
Figure 6.17 Evaluation of J-V characteristics of glass/FTO/CdS/AgSbS <sub>2-x</sub> Se <sub>x</sub> /C/Ag 122
Figure 6.18 Schematic representation of photodetector in photovoltaic mode
Figure 6.19 Photoresponse of the device (photovoltaic mode) illuminated with a) LEDs of
wavelengths 465 (blue), 520 (green) and 590 nm (yellow) b) solar simulator (1000 W/m <sup>2</sup> ).
Figure 6.20 Self-powered photodetection (photovoltaic mode) for 532 nm laser a) different
powers and b) cyclic response, 785 nm laser c) different powers and d) cyclic response. 125
Figure 6.21 Plot of responsivity vs laser power density a)532 nm b)785 nm laser; (c,d) power
law fitting of photocurrent vs incident power density
Figure 6.22 Self-powered photodetection (photovoltaic mode) for lasers (405 nm, 840 nm
and 1064 nm) at zero bias
Figure 6.23 Wavelength vs photocurrent for different lasers
Figure 6.24 CdS/AgSbS <sub>2-x</sub> Se <sub>x</sub> in photoconductive mode
Figure 6.25 Photocurrent response of self-powered photodiodes (photoconductive mode) to
different LEDs a) 350 °C (AgSbS <sub>0.66</sub> Se <sub>1.34</sub> ) b) 375 °C (AgSbS <sub>0.70</sub> Se <sub>1.30</sub> ) heated samples. 129
Figure 6.26 Photoresponse of photodiode (photoconductive mode) (AgSbS <sub>2-x</sub> Se <sub>x</sub> heated at
350 °C and 375 °C) with different laser powers (a,b) 532 nm laser, (c,d) 785 nm laser, cyclic
response to (e,d) 532 nm ,(g,h) 785 nm lasers
Figure 6.27 Sensitivity vs laser power density plot for photodiodes (photoconductive mode)
with a) 532 b) 785 nm lasers
Figure 6.28 Responsivity vs power density plot for photodiodes (photoconductive mode)
with a) 532 and b) 785 nm laser
Figure 6.29 XRD patterns of AgSbS <sub>2-x</sub> Se <sub>x</sub> :Graphene films

Figure 6.30 Raman spectra of AgSbS<sub>0.40</sub>Se<sub>1.60</sub>, AgSbS<sub>0.30</sub>Se<sub>1.70</sub> and AgSbS<sub>0.20</sub>Se<sub>1.80</sub> thin films. Figure 6.31 XPS high resolution spectra of (a-c) Ag 3d, (d-f) Sb 3d, (g-i) S 2p, (j-l) Se 3d and (m-o) C 1s in AgSSSe+G1, AgSbSSe+G3 and AgSbSSe+G5......137 Figure 6.32 SEM images of a) AgSSSe+G1 (AgSbS<sub>0.40</sub>Se<sub>1.60</sub>) b) AgSbSSe+G3 Figure 6.33 a) Transmittance and reflectance b) absorption spectra and c) Tauc plots of AgSbSSe+G1(AgSbS<sub>0.40</sub>Se<sub>1.60</sub>), AgSbSSe+G3 (AgSbS<sub>0.30</sub>Se<sub>1.70</sub>) and AgSbSSe+G5 Figure 6.34 Photocurrent response of AgSbSSe+G1 (AgSbS<sub>0.40</sub>Se<sub>1.60</sub>), AgSbSSe+G3 (AgSbS<sub>0.30</sub>Se<sub>1.70</sub>) and AgSbSSe+G5 (AgSbS<sub>0.20</sub>Se<sub>1.80</sub>) thin films......140 Figure 6.35 a) schematic of solar cells b) J-V plots of Glass/FTO/CdS /p-AgSbS<sub>2-x</sub>Se<sub>x</sub>/C/Ag Figure 6.36 Schematic illustration of CdS/AgSbS<sub>2-x</sub>Se<sub>x</sub>:Graphene self-powered photodiode Figure 6.37 Photocurrent response of photodiodes (photovoltaic mode) fabricated with AgSbSSe+G1 (AgSbS<sub>0.40</sub>Se<sub>1.60</sub>), AgSbSSe+G3 (AgSbS<sub>0.30</sub>Se<sub>1.70</sub>) and AgSbSSe+G5 Figure 6.38 The photocurrent response of photodiodes (photovoltaic mode) under 532 nm laser with different laser powers and the corresponding cyclic measurements (50 mW) (a and b) AgSbSSe+G1 (AgSbS $_{0.40}$ Se $_{1.60}$ ), (c and d) AgSbSSe+G3 (AgSbS $_{0.30}$ Se $_{1.70}$ ), (e and f) Figure 6.39 The photocurrent response of photodiodes (photovoltaic mode) under 785 nm laser with different laser powers and the corresponding cyclic measurements (50 mW) (a and b) AgSbSSe+G1 (AgSbS<sub>0.40</sub>Se<sub>1.60</sub>), (c and d) AgSbSSe+G3 (AgSbS<sub>0.30</sub>Se<sub>1.70</sub>), (e and f) Figure 6.40 Sensitivity of CdS/AgSbS<sub>2-x</sub>Se<sub>x</sub>:Graphene photodiodes (photovoltaic mode) towards different laser powers a) 532 nm b) 785 nm. ..... 147 Figure 6.41 Responsivity of CdS/AgSbS<sub>2-x</sub>Se<sub>x</sub>:Graphene photodiodes (photovoltaic mode) 

# List of tables

Table 4.1 Microstrain, dislocation density and crystallite size of the thin films. Repr	oduced
with kind permission from Elsevier[109]	44
Table 4.2 Hall coefficient, carrier concentration, hall mobility and conductivity va	lues of
AgSS50, AgSbS60, AgSbS80, AgSbS100 and AgSbS110 thin films. Reproduced wi	th kind
permission from Elsevier[109].	57

Table 5.1 Binding energy values of Ag, Sb, S and Se74
Table 5.2 EDX analysis to show the atomic percentage of each element present in thin films.
Table 5.3 Carrier concentration, Hall mobility and conductivity values of AgSbS <sub>2-x</sub> Se <sub>x</sub> films.
Table 5.4 $I_{\lambda_1}$ sensitivity and responsivity obtained for AgSbS <sub>2-x</sub> Se <sub>x</sub> samples with different
LEDs and laser powers. Reproduced with kind permission from Elsevier [109]94
Table 5.5 Photovoltaic parameters of AgSbS2-xSex solar cells.    98
Table 5.6 Photovoltaic parameters of AgSbS2-xSex solar cells.       99
$Table \ 5.7 \ Photos ensitivity \ values \ of \ AgSbS_{1.28}Se_{0.72} \ photodiode \ under \ different \ light \ sources.$

Table 6.2 Photovoltaic parameters of the solar cells.	
Table 6.3 Sensitivity values of AgSbS <sub>2-x</sub> Se <sub>x</sub> self-powered photodiode using Ll	EDs of different
wavelength and solar simulator.	

Table 6.4 Sensitivity, responsivity and detectivity of AgSbS <sub>2-x</sub> Se <sub>x</sub> photodiode i	lluminated
with 532 and 785 nm lasers of different powers	
Table 6.5 Photovoltaic parameters of AgSbS <sub>2-x</sub> Se <sub>x</sub> :Graphene solar cells	141
Table 6.6 Sensitivity values of FTO/CdS/AgSbS <sub>2-x</sub> Se <sub>x</sub> :Graphene photodiodes	144

### Abbreviations

AFM: Atomic Force Microscopy AgSbS<sub>2</sub>: Silver antimony sulfide AgSbS<sub>2-x</sub>Se<sub>x</sub>: Silver antimony sulfoselenide AgSbSe<sub>2</sub>: Silver antimony selenide a-Si: Amorphous Si **BE:** Binding energy CBD: Chemical bath deposition CBM: Conduction band minimum CdS: Cadmiun sulfide CdTe: Cadmium telluride CIGS: Copper indium gallium di selenide CZTS: Copper zinc tin sulfide DW: Distilled water EDX: Energy Dispersive X-Ray FF: Fill factor FTO: Fluorine doped tin oxide GIXRD: Grazing incidence XRD IPA: Isopropyl alcohol ITO: Indium doped tin oxide JCPDS: Joint Committee on Powder **Diffraction Standards** Jsc: Short circuit current density J-V: Current density: voltage LED: Light emitting diode PCE: Power conversion efficiency **PV:** Photovoltaics Sb<sub>2</sub>S<sub>3:</sub> Antimony sulfide SCAPS-1D: Solar Cell Capacitance Simulator-1 dimensional software

SEM: Scanning Electron Microscopy TCO: Transparent conductive oxide TEM: Transmission Electron Microscopy UV-Vis-NIR: Ultraviolet-Visible-Near Infrared VASP: Vienna Ab-initio Simulation Package VBM: Valence band maximum Voc: Open circuit voltage W-H: Williamson- Hall XPS: X-Ray Photoelectron Spectroscopy XRD: X-Ray diffraction

### CHAPTER 1 THIN FILM SOLAR CELLS

Conventional energy sources such as fossil fuels, coal and gas are being used by the world for a long time. However, use of these sources has made a lot of negative impacts on environment such as global warming, air pollution and acid rain [1]. Solar energy is the most powerful and abundant renewable energy source available on the earth that can satisfy the rising global energy demand. In general, solar cell is a p-n junction that converts sun light into electrical energy. The photovoltaic effect is the basic principle behind the production of electricity from solar radiation. Electrons and holes are generated in the semiconductor when the sunlight falls on it. The photoexcited carriers are separated by the electric field present at the p-n junction. These carriers are collected by electrodes present at both n and p sides of the semiconductor [2].

The first, second and third generations are the three different classification of solar cells depending upon the absorbing material used [3,4]. The conventional solar cell uses Si wafers as the absorbing material, which is termed as first generation solar cells. The mono crystalline and polycrystalline Si fall under this category. However, the high cost of production is a major concern [2,5] and hence parallel technologies are always welcome.

Second generation solar cells are generally known as thin film solar cells. These types of solar cells are fabricated by depositing thin layers of photovoltaic material. The advantage of this technology includes lesser material usage, low weight of solar cells due to the usage of thinner layers (nano meters to tens of micrometers) and less manufacturing cost. The second generation can be classified in to amorphous Si (a-Si), cadmium telluride (CdTe) and copper indium gallium di selenide (CIGS) [6]. Compared to Si solar cells these are cheaper and can absorb light at higher rates (around 10-100 times more) [7].

Thin film technology with emerging photovoltaic materials, which still need demonstration and research belong to third generation solar cells [8]. Most of the developed third generation solar cells are copper zinc tin sulfide (CZTS), organic solar cell, perovskite and dye-sensitized solar cells [3]. These solar cells are currently more in demand than first-

and second-generation solar cells because of their low cost and ease of production. The development of low-cost materials and enhancing the stability of third generation solar cells are the key areas of today's research. The efficiency and production cost comparisons of first, second and third generation solar cells is given in figure below [9].



Figure 1.1 Efficiency and cost comparison of different photovoltaic technologies [9].

#### 1.1 Thin film solar cells

The thin film solar cells consist of different layers of materials in the form of thin films. Thin film heterojunction solar cells which are made from two different materials viz absorber and buffer which constituting a heterojunction. The absorber material should have an ideal bandgap around 1.4 eV [10] and the buffer (window) layer generally n type should have a bandgap about 2.4 or > 2.4 eV [11]. The basic structure of a thin film solar cell is given in Figure 1.2a, comprising a substrate, a front contact formed mostly of transparent conductive oxide (TCO), a window layer, an absorber layer, and a back contact that is primarily a metal contact. The work function of the metals used as the back contact should be greater than that of the absorber material. Materials used as back contact include Mo, Ag, and Au. TCOs are used as front contact [12]. As TCOs in solar cells, n-type semiconductor materials with broad bandgaps (>3.3 eV) are typically utilized. Examples of these materials are CdSnO<sub>4</sub>, fluorine-doped SnO<sub>2</sub> (FTO), and indium-doped SnO<sub>2</sub> (ITO). These materials exhibit high transparency

in the visible range and good electrical conductivity [11]. In a solar cell, a window layer's function is to join an absorber layer at the junction while allowing the most of the light possible to enter. In thin film solar cells, a buffer layer is utilized to reduce absorption losses and move produced carriers from absorber to electrode. The performance of heterojunction solar cell is mainly dependent on absorber material, such that direct bandgap semiconductor materials having high absorption coefficient are chosen. The current density voltage characteristics of the device under dark (without illumination) and under illumination are presented in Figure 1.2b [13].

As we explained earlier, the basic principle of solar cells is based on the photovoltaic effect. Electron-hole pairs are created at the junction when the light with a photon energy larger than semiconductor's bandgap strikes on it. Further, the internal electric field present separates the generated electrons and holes into the external circuit without recombining with one another for the photovoltaic effect to occur. The photogenerated electron travels to the junction's n-side, while the hole travels to the p-side. If the carriers are produced outside of the p-n junction's depletion area, thermal diffusion help them to get there. Minority charge carriers from the p-side (electrons) will migrate towards the n-side, leaving a hole in the pregion, while minority charge carriers from the n-side (holes) will move towards the p-side, leaving an electron in the p-region. Thus, a potential difference between the p and n regions of the junction is produced, and this phenomenon is known as the photovoltaic effect. Under short-circuit conditions, such a flow of carriers into the external circuit creates a reverse electrical current density, or short circuit current density (J<sub>sc</sub>). Different parameters, including current density at maximum power point (J<sub>mp</sub>), voltage at maximum power point (V<sub>mp</sub>), shortcircuit current density (J<sub>sc</sub>), and open circuit voltage (V<sub>oc</sub>) can be calculated from the J-V characteristics of solar cells [14,15]. The J-V curves of solar cell under dark and illumination conditions are presented in Figure 1.2b. The circuit diagram corresponding to a solar cell is given in Figure 1.2c. The circuit consists of a current source, one diode, a series  $(R_s)$  and parallel resistance ( $R_{sh}$ ).



Figure 1.2 a) Schematic illustration of thin film solar cells b) J-V characteristics of solar cell under dark and illumination [13] c) equivalent circuit of a solar cell.

#### **1.1.1 Amorphous silicon**

Amorphous Si solar cells (a-Si) have gained great attention in the field of thin film PV due to their low cost of production compared to crystalline solar cells (c-Si) [3]. In addition to having a higher absorption coefficient that enables greater solar radiation absorption. These materials are composed of randomly oriented Si atoms in a homogenous layer instead of crystal structure. Due to the presence of dangling bonds, amorphous Si lack long range crystalline order [16]. These dangling bonds supply the locations for the recombination of electrons and holes, after which they are passivated with hydrogen to form hydrogenated a-Si (a-Si:H). However, these bonds and the mobility of hydrogen will cause the solar cell to become unstable, lowering its efficiency during the first few hours when exposed to sunlight. This effect is known as Stabler-Wronski effect. Solar cells with multi junction structures using intrinsic materials of different bandgaps can reduce this light

induced degradation by providing wider spectrum [17,18]. Recently reported triple junction solar cells with top layer a-Si, middle layer of a-SiGe:H with a bandgap of 1.6 eV and bottom layer of a-SiGe:H with bandgap 1.4 eV have resulted in an efficiency of 13% [17]. Researchers are currently working on p-i-n stacked amorphous Si solar cells to produce more efficient solar cells by using high quality wide bandgap materials.

#### **1.1.2 Cadmium telluride**

Cadmium telluride is one of the leading thin film PV technologies in the global market after crystalline solar cells. Direct bandgap of 1.45 eV, high absorption coefficient, and chemical stability are some of the key characteristics of CdTe as a photovoltaic material [5,19–21]. In the year 1972, Bonet and Rabenhorst produced the first CdTe solar cells. A three-step procedure was used to create the CdS/CdTe heterojunction, which had a 6% efficiency [22]. Several procedures have been implemented to increase the efficiency of CdTe based solar cells, such as high temperature CdTe deposition, CdCl<sub>2</sub> activation treatment, Cu doping, etc., which together produced a conversion efficiency of 15%. Wu et. al. at the National Renewable energy laboratory were able to increase efficiency by 16.5% [23]. By implementing novel methods including bandgap grading and copper embedding, the efficiency of CdTe solar cells has significantly improved during the last five years. An efficiency of 21.5% was achieved as a result of these changes [24]. Toxicity and scarcity of cadmium present major environmental problems. These issues motivated scientists to explore for new, innovative materials that were devoid of toxicity and elemental scarcity.

#### 1.1.3 Copper indium selenide (CIS) and copper indium gallium selenide (CIGS)

CuInSe<sub>2</sub>, often known as CIS, is a ternary compound that forms tetragonal chalcopyrite crystals and is a member of the I-III-VI<sub>2</sub> family. In 1976, the first CIS/CdS solar cell was made by evaporating CuInSe<sub>2</sub> in the presence of Se powder, which produced a 4-5% efficiency [25]. Through the co-evaporation of elemental sources, Mickelson and Ken created CIS solar cells in 1981 with a 9.4 % efficiency [26]. Alloying with Ga resulted in copper indium gallium selenide (CIGS). This has a direct bandgap of 1-1.2 eV with high absorption coefficient  $(10^5 \text{cm}^{-1})[10,27-30]$ . Electrodeposition process is typically used to create CIGS solar cells on a wide scale [3]. Due to extensive research and development the best cell efficiency reported so far is 22.6% [31]. The maximum theoretical efficiency that can be acquired using CIGS is 33.5% with a bandgap of 1.4 eV [32]. The efficiency

improvements are being made in a variety of ways, such as by increasing the CIGS absorber layer's absorption by doping, which raises the Jsc value, or by surface passivation etc. In CIGS, the cell efficiency is decreased by mid gap defects and discontinuities at the interface. In addition, a significant problem with CIGS solar cells is the toxicity and scarcity of In and Ga.

The certified efficiencies of various photovoltaic technologies by NREL are given in Figure 1.3



Figure 1.3 Certified efficiencies of different solar cells, NREL <u>https://www.nrel.gov/pv/cell-</u> <u>efficiency.html</u> (accessed November 23 2022).

#### 1.2 Emerging thin film solar cells

#### 1.2.1 Dye-Sensitized solar cells (DSSC)

DSSCs are third generation solar cells that have a thin semiconductor layer formed between a photosensitized anode and electrolyte [33,34]. Unlike other PV technologies that use semiconductor in the solid form, DSSCs absorb photons using a photosensitizer. In DSSCs liquid electrolytes are used to transfer ions to counter electrode leading to the production of electric current [35]. The breakthrough in DSSC happened in 1991, when Oregan and Gratzel developed a 7.1% efficient solar cell. With a current efficiency of 13.6%,

DSSCs are a possible replacement for Si solar cells due to their low production costs, simple structure and readily available materials. Electrons are introduced into the mesoporous oxide film's conduction band when sunlight strikes the DSSC sensitizer [33]. The produced electrons finally diffuse into anode and end the cycle.

#### 1.2.2 Organic and polymer solar cells

Organic solar cells contain small organic molecules or polymers which absorb light [36,37]. Since there is no production of charge carriers in organic solar cells, their operating process differs from that of inorganic solar cells. They are made up of electron donor and acceptor materials, where the donor absorbs solar photons, and the acceptor creates and confines excitons. By use of effective electric fields, the acceptor material absorbs the electrons that are separated from electron-hole pairs [34,38].

#### **1.2.3 Perovskite solar cells**

Perovskites have a basic crystal structure ABX<sub>3</sub>, where A and B are cations and A is an anion species [39]. Perovskite materials have high carrier mobility, minimal recombination losses and large absorption coefficient [40]. An organic-inorganic active layer made of lead or tin halide serves as the light-harvesting component of PSCs' fundamental structure. When the absorber layer in PSCs absorbs light excitons are produced. These excitons migrate to donor/acceptor (D/A) interface by diffusive process, in which they move from high to low exciton concentration. They undergo dissociation to create free charges at the D/A interface. Through the electron transport layer, the electrons arrive at the cathode [41]. The first perovskite solar cell was demonstrated by Miyasaka in 2009, with an efficiency of 3.81% [42]. Since then, after many surprising breakthroughs, PSCs have reached an efficiency of 23.3%. However, there are some factors that restrict the commercialization of PSCs such as, poor structural stability, they are extremely sensitive to water, heat, and oxygen environments. In addition, difficulty in large area preparation and use of toxic elements like lead [42].

#### **1.2.4 Copper Zinc Tin Sulfide (CZTS)**

CZTS is an emerging material in PV due to the presence of less toxic, low cost and earth-abundant constituent elements [43–45]. It is comparable to CIGS, which was created by substituting group II and IV, Zn and Sn atoms for group III elements In/Ga [46]. CZTS is a quaternary semiconductor with a direct bandgap of 1.45-1.6 eV [47,48]. The highest
theoretical efficiency of CZTS solar cells according to Schockley-Queisser limit is 34% [49]. A 0.66 % efficient CZTS solar cells were prepared by Katagiri and coworkers through sputtering process [50]. Later Shin achieved 8.4% efficient cells by vacuum processing [51]. According to recent research, the Cu<sub>2</sub>ZnSn(S<sub>x</sub>Se<sub>1-x</sub>)<sub>4</sub> alloy (CZTSSe) formed when Se was incorporated into CZTS improved the device's characteristics [52,53]. The structural and opto-electronic properties of the compound change with variation in S/Se ratio [54]. The highest efficiency reported so far for CZTSSe solar cell with S/[S+Se] ratio of about 30 % is 12.6% [55]. The major factor that influence the CZTS cell efficiency is cation disorder defects, which will reduce open circuit voltage hence the reduction in solar cell efficiency [56].

#### 1.2.5 Antimony sulfide (Sb<sub>2</sub>S<sub>3</sub>) and antimony sulfoselenide (Sb<sub>2</sub>(S<sub>1-x</sub>Se<sub>x</sub>)<sub>3</sub>

Sb<sub>2</sub>S<sub>3</sub> is one of the emerging chalcogenides for photovoltaic applications, with a bandgap of 1.7 eV and a strong absorption coefficient (>10<sup>4</sup> cm<sup>-1</sup>) that are composed of nontoxic and earth abundant elements [57–60]. It is a stable binary compound with a melting point of ~ 550 °C. There are various methods to synthesis Sb<sub>2</sub>S<sub>3</sub> thin films which include, spray pyrolysis, chemical bath deposition method [61,62], dip-dry [63] method and thermal evaporation [64]. Solution processed Sb<sub>2</sub>S<sub>3</sub> solar cells have reported ~7.5% [65] efficiency. Sensitized solar cells fabricated by solution-based technology have PCE of 6.4%. According to Schokley-Queisser limit Sb<sub>2</sub>S<sub>3</sub> can achieve a maximum efficiency of 28.64 % with a bandgap of 1.7 eV [66]. Although it is a new PV material, its high resistivity restricts short circuit current density and fill factor values.

The bandgap tuning in Sb<sub>2</sub>S<sub>3</sub> can be done by incorporating Se to produce Sb<sub>2</sub>(S<sub>x</sub>Se<sub>1-x</sub>)<sub>3</sub> [67–69]. The bandgap value can be varied from 1.1 to 1.8 eV by changing S and Se contents [70]. According to Shockley-Queisser theory the most suitable bandgap for photovoltaic application is around 1.3 eV, so Sb<sub>2</sub>(S<sub>x</sub>Se<sub>1-x</sub>)<sub>3</sub> with proper bandgap by varying the components will be an optimal choice for PV application.

#### **1.2.6** Copper antimony sulfide (CuSbS<sub>2</sub>)

Ternary CuSbS<sub>2</sub> has been proposed as a novel chalcogenide photovoltaic material due to the earth abundant and non-toxic elements, suitable bandgap (1.5 eV), high absorption coefficient ( $10^4$  cm<sup>-1</sup>) and p-type conductivity [71–74]. Only a few publications describe how CuSbS<sub>2</sub> thin films can actually be used as solar cells, despite the fact that several

investigations have been done on the materials' characteristics and their application as absorbers [75–77]. Nair et al. carried out the ground-breaking research on this material, creating CuSbS<sub>2</sub> absorber layers by heating chemically produced Sb<sub>2</sub>S<sub>3</sub>-Cu<sub>2</sub>S layers. With a CdS window layer and Sb<sub>2</sub>S<sub>3</sub> intrinsic layer, a PV device was constructed that had J<sub>sc</sub> of 0.2 mA/cm<sup>2</sup> and V<sub>oc</sub> of 345 mV [71,72,78]. Generally, CuSbS<sub>2</sub> can be deposited by physical as well as chemical methods, which include co-evaporation of Cu, Sb and S pure elements, thermal evaporation of CuSbS<sub>2</sub> powder, co-RF sputtering of the respective targets (Sb<sub>2</sub>S<sub>3</sub> and Cu<sub>2</sub>S), electrodeposition of Sb-Cu alloys over S, chemical bath deposition, spin coating of precursor solution, spray pyrolysis [51,79–81] etc. CuSbS<sub>2</sub> solar cell fabricated by heating Sb<sub>2</sub>S<sub>3</sub>-Cu stack layers resulted a highest V<sub>oc</sub> of 665 mV and FF of 0.6 [77]. The best efficiency for this material so far has been reported by Banu et al. in 2016 is 3.22% with a V<sub>oc</sub> of 470 mV [72]. Because of defects in the absorber layer and interfacial recombination of minority carriers, the efficiency of CuSbS<sub>2</sub> PV devices is limited [82].

# 1.2.7 Silver antimony sulfide, selenide and sulfoselenide

Among these emerging chalcogenides, AgSbSe<sub>2</sub> is known for its outstanding thermoelectric performance with ultralow thermal conductivity and narrow bandgap [83]. Its thermoelectric performance can be further enhanced by doping with various elements [84–86] to increase p-type carriers. Experimentally, both direct and indirect optical bandgaps were reported in AgSbSe<sub>2</sub> with p-type conductivity [87–89], higher values than that of a thermoelectric material. Electrodeposited AgSbSe<sub>2</sub> displayed a direct band gap of 1.18 eV [83]. The thin films formed by the direct mixing of their constituent elements were reported to have an indirect bandgap value of 0.93 eV [88]. The first AgSbSe<sub>2</sub> solar cells were fabricated by heating chemically deposited Sb<sub>2</sub>S<sub>3</sub> and thermally evaporated Ag stack layers in contact with selenium films produced by a solution technique [90].

AgSbS<sub>2</sub> films belong to I-V-VI<sub>2</sub> ternary chalcogenide group [91]. The mostly reported structures of AgSbS<sub>2</sub> are monoclinic [92,93] and cubic [94]. Nabil Hosni reported monoclinic AgSbS<sub>2</sub> with a direct band gap of 1.65 eV and an absorption coefficient of  $10^4$  cm<sup>-1</sup> [95]. Further, the AgSbS<sub>2</sub> silk-like nano flowers showed broad absorption and high value of incident photon to current efficiency (IPCE) in the visible range [96]. A photovoltaic device used the AgSbS<sub>2</sub> film created by an in-situ gas-solid reaction on TiO<sub>2</sub> layer. Over the spectrum range of 300-700 nm, the device demonstrated strong photoresponse and an average

external quantum efficiency (EQE) of 15% [97]. Jesus Capistran reported the solar cells made from the AgSbS<sub>2</sub> absorber layer, which showed an efficiency of 0.57 %. By assembling AgSbS<sub>2</sub> nanoparticles made using the double-step SILAR technique over sensitized TiO<sub>2</sub> electrode, Yi-Rong was able to create wet chemically AgSbS<sub>2</sub> semiconductor sensitive solar cells. The photodetector device fabricated with in-situ-gas solid reacted AgSbS<sub>2</sub> showed high photoresponse value. The dye-sensitized AgSbS<sub>2</sub> liquid junction solar cells showed an enhanced photovoltaic property, with PCE of 1.28 % [98].

Silver antimony sulfoselenide solid solution thin films are another emerging metal chalcogenide composed of earth abundant, nontoxic elements. The property of these materials can be spanned between that of pure AgSbSe<sub>2</sub> and AgSbS<sub>2</sub>. AgSbSe<sub>2</sub> or AgSbS<sub>2</sub> solar cells have not yet been able to achieve a considerable efficiency value (>3%). By adjusting the Se/S ratio in the compound, the bandgap of the material can be modified. AgSbS<sub>2-x</sub>Se<sub>x</sub> with proper components might be a good choice for photovoltaic applications. However, only limited reports are available in the literature related to this material. AgSb(S<sub>x</sub>Se<sub>1-x</sub>)<sub>2</sub> based solar cells using CdS as a window layer showed better photovoltaic characteristics [99], the best cell giving a PCE of 2.77% [100]. Recently silver antimony sulfide selenide deposited by chemical deposition technique resulted in an efficiency of 0.65% [101]. More efforts are essential towards systematic studies to improve the optoelectronic properties of this material and thus their device efficiency.

# **1.3 Hypothesis**

High quality silver antimony sulfoselenide solid solution thin films with tunable optoelectronic properties can be formed by varying Ag/Sb and S/Se ratios in the precursors to produce solar cells with high efficiency.

# **1.4 Objectives**

# 1.4.1 General objective

To develop highly efficient solar cells using silver antimony sulfoselenide thin films as absorber material.

# **1.4.2 Specific objectives**

- Synthesis of silver antimony sulfo-selenide thin films
- Analysis of structure, morphology and composition of AgSbS<sub>2-x</sub>Se<sub>x</sub> thin films
- Evaluation of optical and electrical properties of AgSbS<sub>2-x</sub>Se<sub>x</sub> thin films
- Theoretical analysis based on density functional theory (DFT).
- Varying of optical and electrical properties of AgSbS<sub>2-x</sub>Se<sub>x</sub> by changing Ag/Sb and S/Se ratio
- Fabrication and evaluation of photovoltaic properties of AgSbS<sub>2-x</sub>Se<sub>x</sub> solar cells
- Further control of Se in AgSbS<sub>2-x</sub>Se<sub>x</sub> thin films using Se nanocolloids
- Studies on the effects of Se nanocolloids on films
- Studies on effects of post deposition and contact types on the PV properties.

# **1.5 Justification**

To produce cost-effective thin film solar cells, the appropriate choice of absorber the layer is very important. An intense investigation has been in progress to produce novel materials as absorber layers, which include chalcogenides such as Cu (In Ga) Se<sub>2</sub> and CdTe. But the main disadvantages of these materials are the toxicity of cadmium and scarcity of indium, gallium, and tellurium, so to satisfy the world's energy demand, we need to look for new materials that are free from toxicity and scarcity of elements. Silver antimony sulfo-selenide thin film is an emerging material for photovoltaic applications, due to the presence of non-toxic and earth abundant elements. The material also possesses high absorption coefficient ( $^{10^5}$  cm<sup>-1</sup>) and bandgap value of 1.1-1.6 eV an ideal value for solar cell applications. However, only a few studies are available related to this material. Hence, this thesis is mainly focused on the synthesis, characterization, and photovoltaic and photodetector applications of AgSbS<sub>2</sub> and AgSb(S<sub>2-x</sub>Se<sub>x</sub>) thin films. In addition, theoretical studies based on density functional theory (DFT) and SCAPS are also presented here.

# CHAPTER 2 THEORETICAL STUDIES

This chapter describes the theoretical calculation details of AgSbS<sub>2</sub> and AgSbS<sub>2-x</sub>Se<sub>x</sub> crystals. The crystal structure, band structure and density of states calculations using VASP (Vienna Ab-initio Simulation Package) code implemented in MedeA software are presented. We also present simulation studies of FTO/CdS/AgSbS<sub>2-x</sub>Se<sub>x</sub>/Ag solar cells using Solar Cell Capacitance Simulator-1 dimensional software (SCAPS-1D).

# **2.1 VASP**

Computational analysis was done for monoclinic as well as cubic AgSbS<sub>2</sub>, and AgSbSe<sub>2</sub>. For this, the crystal structure calculations are performed by VASP implemented in MedeA software [102,103], in which projected augmented wave (PAW) method is used [104]. The calculation is schematically represented in flow chart below.



Figure 2.1 Calculation flow chart of VASP.

To determine the ground state structure, the crystal structure optimization for monoclinic  $AgSbS_2$  was done using Perdew-Burke-Ernzerhof generalized gradient approximation formulated for properties of solids (GGA-PBEsol) [105]. To relax atomic positions and lattice parameters, the cut-off energy of the system was fixed at 500 eV until

the force and energy converge to 0.02 eV/Å and  $1\times10^{-5}$  eV respectively. Monkhorst-Pack scheme k-point sampling with  $3\times3\times1$  meshes is employed to perform Brillouin zone integration. The linear tetrahedron with Blöchl corrections to the energy is applied for smearing. The optimized structure is used for the band structure and density of states (DOS) calculations by Heyd-Scuseria-Ernzerhof hybrid functional (HSE06) [106] with a cut-off energy of 300 eV and an energy convergence of  $1\times10^{-3}$  eV.

In the cubic systems of AgSbS<sub>2</sub> and AgSbSe<sub>2</sub>, due to the partial occupancy of Ag and Sb atoms, first the structures with Fm-3m space group from the database were converted into  $2\times2\times2$  supercells with equal number of Ag and Sb atoms, a total of 125 atoms/cell. The supercell was chosen such that lattice parameter coincides with our experimental results from XRD. Then AgSbS<sub>2</sub> and AgSbSe<sub>2</sub> supercell structures are optimized using GGA-PBEsol and for both the compounds the cutoff energy was set at 300 eV. The force and energy convergence values were 0.02 eV/Å and  $1\times10^{-3} \text{ eV}$ .  $2\times2\times2$  k-point meshes are used for performing Brillouin zone integration along with Gaussian method for smearing. The optimized AgSbS<sub>2</sub> and AgSbSe<sub>2</sub> structures are used for band structure and density of states calculations by applying GGA-PBEsol.

### 2.1.1 CRYSTAL STRUCTURE

#### Monoclinic AgSbS<sub>2</sub>

The monoclinic AgSbS<sub>2</sub> obtained after the structure optimization is given in Figure 2.2. Monoclinic AgSbS<sub>2</sub> is crystalized in C2/c space group, with Ag atoms connected through chains of SbS<sub>3</sub> pyramids [107]. The obtained lattice parameters are, a = 12.7280 Å, b = 4.270 Å, and c = 13.120 Å, which is in accordance with the original values a = 12.860 Å, b = 4.410 Å, and c = 13.220 Å. In the crystal, Ag atoms occupy at 4e and 4b Wyckoff positions, Sb and S at 8f Wyckoff position. The crystal structure view along (400), ( $\overline{3}12$ ) and ( $\overline{1}15$ ) planes is given in Figure 2.2b-d respectively.



Figure 2.2 a) Unit cell of monoclinic AgSbS<sub>2.</sub> Reproduced with kind permission from Elsevier [108] b) (400) c) ( $\overline{3}12$ ) d) ( $\overline{1}15$ ) planes along c axis [109].

# Cubic AgSbS<sub>2</sub> and AgSbSe<sub>2</sub>

The optimized  $AgSbS_2$  supercell structure with space group P1 is given in Figure 2.3a. From the supercell structure, the lattice parameters were found to be a=b=c=5.550 Å and the values calculated from standard cubic  $AgSbS_2$  is a=b=c=5.652 Å. The Ag atoms

occupy 2c and 2f, Sb atoms 2d and 2a, S atoms occupy 4i, 2b and 2a Wyckoff positions. Further, the optimized structure was used for density of states and band structure calculations. The optimized supercell structure of AgSbSe<sub>2</sub> is the same as AgSbS<sub>2</sub> as given in Figure 2.3a. The obtained lattice parameters were a=b=c=5.662 Å, comparable with that of the standard cubic AgSbSe<sub>2</sub> a=b=c=5.786 Å. The Ag atoms occupy 2c and 2f Wyckoff position, Sb atoms occupy 2d and 2e Wyckoff position, Se atoms at 4i, 2b and 2a Wyckoff positions respectively. The supercell view along (111), (200) and (220) planes is given in Figure 2.3b-d respectively.





Figure 2.3 a)  $2 \times 2 \times 2$  supercell of AgSbS<sub>2</sub>/Se<sub>2</sub> b) (111) c) (200) and d) (220) planes along c axis.

### 2.1.2 Band structure and density of states

The calculated electronic band structure and density of states (DOS) of monoclinic AgSbS<sub>2</sub> are given in Figure 2.4a and Figure 2.4b respectively. The electronic band structure discloses the type of bandgap of the material and the density of states gives the contribution of atomic orbitals towards the valence band maximum (VBM) and conduction band minimum (CBM). Figure 2.4a indicates that the valence band maximum is located at  $\Gamma$  (0 0 0) point with energy level E = -0.081 eV and conduction band minimum at (-0.33 0.33 0) away from  $\Gamma$  point with energy level E = 1.69 eV with respect to Fermi level. This implies that the AgSbS<sub>2</sub> has an indirect band transition across a bandgap of 1.77 eV. The total and partial density of states of the compound is given in Figure 2.4b. The contribution towards VBM mainly comes from Ag d and S p orbitals and CBM from S p orbitals.



Figure 2.4  $AgSbS_2$  a) electronic band structure (b) total and partial density of states. Reproduced with kind permission from Elsevier [108].

The band structure of the cubic  $AgSbS_2$  is given in Figure 2.5a. It represents the overlapping of CB and VB with a pseudogap value of ~-0.109 eV indicating metallic behavior. The total and partial density of states obtained are shown in Figure 2.5b. From the figure, the major contribution towards valence band maximum (VBM) is from Ag 4d and S 3p states and the conduction band minimum is constituted by Sb 5p and S 3p states.

As shown in Figure 2.5c band structure of cubic  $AgSbSe_2$  also indicates a pseudogap of ~-0.21 eV. The analysis of PDOS (Figure 2.5d) curves shows that the VBM is mainly formed from Ag 4d and Se 4p and a small contribution from Sb 5p states. The conduction band minimum formed from Sb 5p and Se 4p states.



Figure 2.5 a) Electronic band structure of AgSbS<sub>2</sub> b) Total and partial density of states AgSbS<sub>2</sub> c) Electronic band structure AgSbSe<sub>2</sub> d) Total and partial density of states AgSbSe<sub>2</sub>.

The above results represent that cubic AgSbS<sub>2</sub> and AgSbSe<sub>2</sub> exhibit a pseudogap, which is similar to the results obtained for cubic AgSbTe<sub>2</sub>, AgSbS<sub>2</sub> and AgSbSe<sub>2</sub>[110]. The

FCC structure of AgSbS<sub>2</sub> resulted in pseudogap of -0.8 eV and a small bandgap of 0.07 eV respectively by FP-LAPW method [111]. All these results can be explained based on cationic disorders in the compounds [112,113]. There have been many reports on cation disorder in ABX<sub>2</sub> rock salt structure where A = Ag, Na; B = Sb and X = S, Se, Te [110,114,115]. In ABX<sub>2</sub>, cation lattice is formed by mixing of A/B atoms and the anion lattice by X atoms. In cubic AgSbS<sub>2</sub>/Se<sub>2</sub>, Ag and Sb atoms are disordered on Na site of NaCl structure [116]. The disorder will lead to drop of conduction band minimum and increase in valence band maximum thereby reducing bandgap. The reduction in the bandgap is theoretically explained on the basis of Urbach tails, where valence band features an exponential decaying tail appearing when band dispersion is suppressed as a result of the material disordering [112]. Higher the disorder, which leads to deeper sinks in the bandgap, reaching to metallic nature.

### 2.2 SOLAR CELL CAPACITANCE SIMULATOR-1 DIMENSIONAL (SCAPS-1D)

SCAPS-1D is a one dimensional solar cell simulation program developed by Department of Electronics and Information Systems of the University of Gent [117]. Simulation study is a tool to approximate the output of a solar cell which can help in experimental fabrication of solar cell. In this study we performed the numerical analysis of FTO/CdS/AgSbS<sub>2-x</sub>Se<sub>x</sub>/Ag solar cell device by varying absorber layer thickness and bandgap. From the optimized parameters (bandgap and thickness) the maximum possible efficiency of the AgSbS<sub>2-x</sub>Se<sub>x</sub> solar cell was calculated. The solar cell configuration is given in Figure 2.6. In this structure FTO has been taken as the front contact, CdS as the window layer, AgSbS<sub>2-x</sub>Se<sub>x</sub> as the absorber layer and Ag as the back contact. The simulation studies were performed using AM 1.5 G (1000 W/m<sup>2</sup>) spectrum.



Figure 2.6 Solar cell structure.

19

# 2.2.1 AgSbS<sub>2-x</sub>Se<sub>x</sub> solar cells

The effect of absorber layer thickness and bandgap on the performance of the solar cells was studied by fixing the CdS layer thickness as 80 nm. The important material parameters used in the simulation are given in Table 2.1. First, we optimized the absorber layer thickness, knowing the fact the absorber layer thickness is greater than all the other layers and it plays an important role in the solar cell performance. The thickness was varied from 400 to 1000 nm with a step size of 300 nm and the bandgap was fixed ( $E_g = 1.56 \text{ eV}$ ). The J-V curves correspond to absorber layer thickness from 400 to 1000 nm is represented in Figure 2.7a. From the figure, the solar cell efficiency increases with absorber layer thickness, the highest efficiency was obtained for 1000 nm. Figure 2.7b represents the effect of bandgap variation in solar cell performance. The bandgap value was varied from 1 to 1.5 eV by fixing the absorber layer thickness as 400 nm, the highest efficiency was obtained for  $E_g = 1.2 \text{ eV}$ . Further, the film with optimum value of absorber layer thickness (1000 nm) and bandgap (1.2 eV) was selected to calculate the maximum possible efficiency of AgSbS<sub>2-x</sub>Se<sub>x</sub> solar cells. The maximum efficiency obtained was 17.4% for the solar cell, which is also presented in Figure 2.7c.

Parameter	Value
Metal work function (front contact) eV	4.4
CdS thickness (window layer) nm	80 nm
Relative dielectric permittivity	13
CB effective density of states (1/cm <sup>3</sup> )	6×10 <sup>19</sup>
VB effective density of states (1/cm <sup>3</sup> )	6×10 <sup>19</sup>
Electron mobility(cm <sup>2</sup> /Vs)	48
Hole mobility (cm <sup>2</sup> /Vs)	48
Shallow uniform acceptor density NA (1/cm <sup>3</sup> )	1×10 <sup>18</sup>

Table 2.1 Material parameters for the SCAPS-1D.



Figure 2.7 Simulated J-V characteristics using SCAPS (a)  $CdS/AgSbS_{1.28}Se_{0.72}$  single junction solar cells with varying absorber layer thickness and a fixed bandgap of 1.55 eV b)  $CdS/AgSbS_{2-x}Se_x$  with varying bandgap for a fixed thickness of 400 nm c) highest possible efficiency using bandgap 1.2 eV and maximum thickness of 1000 nm.

The photovoltaic parameters corresponding to different conditions are presented in the tables below.

Absorber layer thickness	Voc	Jsc (mA/cm <sup>2</sup> )	FF	Efficiency
(nm) (1.56 eV)	(V)	(%)	<b>(%</b> )	(%)
400	0.722	15.4	74.6	8.3
700	0.740	18.7	76.9	10.6
1000	0.751	20.4	78	12

Table 2.2 Photovoltaic parameters correspond to different absorber layer thickness.

From the Table 2.2 efficiency and other output parameters improve as the thickness of the absorber material rises because it absorbs more long wavelength light, resulting in the production of more electron-hole pairs.

Bandgap (eV), 400 nm	Voc (V)	J <sub>sc</sub> (mA/cm <sup>2</sup> ) (%)	FF (%)	Efficiency (%)
1	0.475	31.5	75	11.2
1.1	0.583	27.9	76.7	12.4
1.2	0.684	24.3	77	12.8
1.3	0.721	21	76.7	11.7
1.4	0.722	18	75.8	9.9
1.5	0.722	15.4	74.6	8.3

Table 2.3 Photovoltaic parameters correspond to varying the bandgap value.

Table 2.3 indicate that the  $J_{sc}$  decrease and  $V_{oc}$  increase with bandgap. Usually lower bandgap materials are used as absorber materials in solar cells, so that it can absorb as much of the solar spectrum, higher  $J_{sc}$  value for lower bandgap can be due to the production of more electron-hole pairs.

Table 2.4 Highest photovoltaic parameters obtained corresponds to absorber layer thickness of 1000 nm and bandgap of 1.2 eV.

	V <sub>oc</sub> (V)	J <sub>sc</sub> (mA/cm <sup>2</sup> )	FF (%)	Efficiency
Thickness - 1000 nm		(%)		(%)
Bandgap - 1.2 eV	0.696	31.7	79.5	17.5

The simulation results show that by increasing the thickness of films with lower band gap (1.2 eV) better performance can be achieved. Overall, simulation studies show the scope of this material to produce devices with high performance using 1-micron films with high crystallinity and lower band gap, by controlling the Se/S ratio at optimum thin film growth conditions.

The crystal structure, density of states and band structure of monoclinic AgSbS<sub>2</sub> and cubic AgSbS<sub>2</sub>/Se<sub>2</sub> structures are studied based on the density functional theory (DFT) using VASP implemented in MedeA software. Lattice parameters and bandgap obtained from the calculations are found to be in good agreement with the original values. Further, simulation studies are done for FTO/CdS/AgSbS<sub>2-x</sub>Se<sub>x</sub>/Ag solar cells using SCAPS-1D. The effect of absorber layer thickness and bandgap on the performance of solar cell is studied. From the

optimized parameters the highest possible theoretical efficiency of  $FTO/CdS/AgSbS_{2-x}Se_x/Ag$  solar cell is calculated, and it is found to be 17.5 %.

# **CHAPTER 3**

# EXPERIMENTAL DETAILS: SILVER ANTIMONY SULFIDES AND SULFOSELENIDES

This chapter describes the experimental details for the synthesis and characterization of silver antimony sulfides and silver antimony sulfoselenides. Further it includes the fabrication and evaluation of photovoltaic devices. In general, the synthesis techniques are CBD, thermal evaporation, spin coating and laser fragmentation. Different techniques are used to study the crystal structure, morphology, elemental composition, optical, and electrical properties of the thin films. The photovoltaic devices are characterized by the J-V characteristics.

# 3.1 Thin film deposition techniques

Thin films of  $AgSbS_2$  and  $AgSbS_{2-x}Se_x$  are deposited on glass substrate by combining solution-based deposition techniques such as chemical bath deposition, spin coating and physical deposition technique such as thermal evaporation method.

# **3.1.1** Chemical bath deposition (CBD)

CBD is the simplest among the chemical deposition techniques for producing large area thin films for solar cell applications [118]. Thin films are synthesized on the substrates immersed in the chemical bath containing the cations and anions composed of the compound semiconductor to be deposited. The deposition occurs when the ionic product exceeds the solubility product. The film thickness and composition can be controlled by varying parameters such as precursor concentration, temperature, pH of the solution and use of complexing agents. The photographs of the CBD are given in Figure 3.1.





# **3.1.2** Thermal evaporation technique

Thermal evaporation technique is used for depositing thin films of pure material, with thicknesses ranging from angstroms to microns. This technique involves the heating of solid material/metal inside a vacuum chamber. The material/metal vapor travels through the vacuum chamber with thermal energy and condensed on the substrate placed above the vapor to form thin films. Typically, this method consists of resistive heating of the filament. The filament material used are referred to as a boat. The substrate surface to be coated will be positioned facing the boat.

In this work we used a thermal evaporator (Torr international, Model No: THE2-2.5 kW-TP) for the deposition of Ag thin films. The evaporating material (Ag wire of purity 99.99%) was placed in the tungsten boat. The boat was heated by applying high current (120 A) and voltage (1V). The evaporation was done under a high vacuum (10<sup>-5</sup> Torr) at a rate of 18 Å/s and the substrates were rotated at a speed of 20 rpm. The deposited film thickness was monitored by a quartz crystal thickness monitor associated with the evaporation system. Deposition of a uniform thin film is one of the main advantages of the thermal evaporation technique. The photograph of the Torr international thermal evaporation system is given in Figure 3.2.



Figure 3.2 Photograph of thermal evaporator (Torr international).

# 3.1.3 Spin coating

Spin coating is a common technique used to apply uniform coating on a flat surface [119]. Typically, the spin coating process involves 4 stages. A dispense stage or deposition, spin up or substrate acceleration stage, spin off and evaporation.

# A dispense stage or deposition

In the initial stage, the solution is deposited onto the substrate using a pipette. There are two methods of deposition, static deposition and dynamic deposition. In the static case the solution is simply deposited onto the stationary substrate, after that the substrate undergoes spinning, whereas in the dynamic case dispensing while the substrate is turning at low speed.

#### Spin up or substrate acceleration stage

In this second phase, the substrate reaches the desired speed. Usually at this stage the solution is expelled from the surface. Even though the fluid may be spinning at a different speed than the substrate initially, in this stage it matches with each other when drag balances the rotational acceleration.

# Spin off

In this stage, the fluid starts to thin. The fluid thinning is dominated by viscous forces and is quite uniform. During flung off, it is possible to see film color change due to interference effects, depending upon the viscosity, and surface tension, difference in coating thickness is observed around the rim of the substrate.

# Evaporation

Substrate spinning at a steady speed and solvent evaporation are the defining features of this phase. In this stage fluid outflow stops and fluid evaporation becomes the dominant process. Depending upon the solvent vapor pressure, solvent volatility and ambient conditions solvent evaporation rate may change.

In this work selenium nanocolloid was deposited by a compact spin coater (Model SP-CY4). The coating was done by applying a small amount of Se nanocolloid (40 ml) onto the substrate and then spinning the substrate at a speed around 500 rpm, accelerated speed of 20 rpm/s and the spin time for single coat was 30 s. The nanocolloid spreads across the substrate as a result of centrifugal force [120]. Until the desired film thickness is achieved, rotation is continued while the fluid spins off the substrate's edges.

26



Figure 3.3 Photograph of compact spin coater system and thin film.

# 3.1.4 Pulsed laser irradiation in liquid

Pulsed laser irradiation in liquid is an efficient technique to synthesis and modify micro and nanomaterials. The photothermal effect caused by a laser beam serves as the fundamental principle of this approach. The important advantages of this technique are the short time of synthesis, site specific photothermal effect which can produce nanomaterials with less energy consumption [121,122]. In the present work we synthesized selenium nanocolloids by laser irradiation in liquid technique. Selenium nanoparticles are formed by laser fragmentation in liquid. A pulsed laser source (Nd:YAG laser, model LQ 929 and 629, SOLAR LASER SYSTEMS) of 532 nm wavelength, frequency of 10 Hz and pulse width of 10 nanoseconds (ns) was used for laser fragmentation. The laser irradiation was done in horizontal configuration, where the dispersion was placed in front of the laser source. For the irradiation experiment, the laser was run in Q switching mode following beam alignment. The mixture was stirred using a magnetic stirrer throughout the irradiation process. The photograph of pulsed lased irradiation technique is given in Figure 3.4.



Figure 3.4 Photograph of pulsed laser irradiation in liquid using ND:YAG laser.

# **3.2** Silver antimony sulfide (AgSbS<sub>2</sub>)

AgSbS<sub>2</sub> thin were prepared by heating glass/Sb<sub>2</sub>S<sub>3</sub>-Ag precursor layers. The antimony sulfide (Sb<sub>2</sub>S<sub>3</sub>) thin films were deposited by chemical bath deposition technique [123]. The bath was prepared by dissolving 0.325 g of antimony chloride (SbCl<sub>3</sub>, 99.99%, Fermont) in 1.2 ml of acetone, followed by adding 12.5 ml of sodium thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O, 99.99%, 1 M) supplied by Fermont and 32.5 ml of deionized water. The glass substrates were well cleaned by sonicating in a soap solution and deionized water respectively for 10 minutes. The cleaned substrates were placed horizontally in the bath and the deposition temperature was 25 °C for 30 minutes.

On the Sb<sub>2</sub>S<sub>3</sub> films, Ag was coated by thermal evaporation technique using Ag wire of purity 99.99% as evaporant. Samples with precursor layer having silver thickness 5, 10, 20, 50, 60, 80, 100 ad 110 nm were synthesized. Silver thickness was measured in-situ using a quartz crystal monitor incorporated in the evaporation system. The Sb<sub>2</sub>S<sub>3</sub>-Ag precursor layers deposited over the glass was heated at 350 °C for 30 minutes in a vacuum chamber (TM Vacuum Products Model No V/IG-803-14 at a pressure of  $10^{-3}$  Torr). The heated samples are identified as AgSbS50, AgSbS60, AgSbS80, AgSbS100 and AgSbS110, where the number corresponds to silver thickness. The schematic representation of AgSbS<sub>2</sub> film formation is represented in Figure 3.5



Figure 3.5 Schematic representation of preparation of AgSbS<sub>2</sub> thin films.

# 3.3 Silver antimony sulfoselenide synthesis (AgSbS<sub>2-x</sub>Se<sub>x</sub>)

In this case, the as-deposited glass/Sb<sub>2</sub>S<sub>3</sub>-Ag films were selenized by a solution method [99] prior to heating. The preparation of Sb<sub>2</sub>S<sub>3</sub>-Ag precursor layers is already explained in section 3.1.1. The Ag thickness varied from 10, 20, 40, 50, 60, 80, 100 and 110 nm. These precursor layers were selenized by dipping in an aqueous sodium selenosulfate (Na<sub>2</sub>SeSO<sub>3</sub>) solution [99] for 10 minutes. The solution was prepared by mixing 1.1 ml acetic acid (25% volume) diluted with 20 ml of deionized water and 20 ml Na<sub>2</sub>SeSO<sub>3</sub> solution (0.016 M). AgSbS<sub>2-x</sub>Se<sub>x</sub> thin films were also prepared by varying the selenization time. Glass/Sb<sub>2</sub>S<sub>3</sub>-Ag precursor layers with 50 and 100 nm silver thickness was dipped in Na<sub>2</sub>SeSO<sub>3</sub> solution for 15, 20 and 30 minutes. Finally, as described in section 3.1.1, glass/Sb<sub>2</sub>S<sub>3</sub>-Ag<sub>2</sub>Se precursor films were heated in a vacuum chamber at 350 °C for 30 minutes. Figure 3.6 shows a schematic of the synthesis of AgSbS<sub>2-x</sub>Se<sub>x</sub>.

# 3.4 Synthesis of Se and Se:Graphene nanocolloid

Selenium nanocolloid was synthesized by pulsed laser irradiation of selenium powder dispersed in distilled water (DW), acetone and isopropyl alcohol (IPA) (Fermont). 20 mg of bulk selenium powder was weighed and added into 40 ml of different solvents such as DW, acetone, and IPA, followed by ultrasonicating for 15 minutes to get uniform dispersion in the liquid. After dispersion the mixture was continuously stirred and irradiated with a laser in horizontal position. We used Nd:YAG laser (model LQ 929 and 629) of 532 nm wavelength, frequency of 10 Hz, pulse width of 10 nanoseconds (ns) and an irradiation time of 20 minutes. After irradiation the mixture was turned into a stable, uniform red color Se nanocolloid.

Se:Graphene nanocolloid was synthesized by directly adding graphene powder to Se nanocolloid synthesized by laser irradiation and then ultrasonicating for 15 minutes. Se:Graphene (Se:G) nanocolloid with different amounts of graphene (1, 3 and 5 mg) was synthesized.

#### 3.5 Preparation of AgSbS2-xSex and AgSbS2-xSex:Graphene thin films

AgSbS<sub>2-x</sub>Se<sub>x</sub> thin films were prepared by heating glass/Sb<sub>2</sub>S<sub>3</sub>-Ag-Se precursor layers. Glass/Sb<sub>2</sub>S<sub>3</sub>-Ag layers were sequentially deposited by chemical bath deposition of Sb<sub>2</sub>S<sub>3</sub> followed by thermal evaporation of Ag as mentioned earlier in section 3.2. The Se nanocolloid synthesized by laser irradiation technique was deposited over the precursor layer by a spin coating technique. A compact spin coater system with a spin speed of 500 rpm, accelerated speed of 20 rpm/s and the spin time of 30 s was used for coating of Se nanocolloid. The precursor layer was heated at 325 °C, 350 °C and 375 °C for 30 minutes in a vacuum oven.

AgSbS<sub>2-x</sub>Se<sub>x:</sub> graphene thin films were synthesized by the same method as mentioned above. Above glass/Sb<sub>2</sub>S<sub>3</sub>-Ag precursor layers Se:Graphene nanocolloid was deposited by spin coating. The precursor layers were heated at 350 °C for 30 minutes in vacuum oven to form AgSbS<sub>2-x</sub>Se<sub>x:</sub>Graphene thin films. The films were labelled as AgSbSSe+G1, AgSbSSe+G3 and AgSbSSe+G5, where G1, G3 and G5 correspond to 1, 3 and 5 mg of graphene. The schematic of thin film formation is given in figure below.



Figure 3.6 Schematic representation for synthesis of AgSbS<sub>2-x</sub>Se<sub>x</sub> thin films.

# 3.6 Device fabrication: solar cells and photodetectors

# 3.6.1 Solar cells: glass/FTO/CdS/AgSbS2/C/Ag and glass/FTO/CdS/AgSbS2- xSex/C/Ag

 $AgSbS_2$  and  $AgSbS_{2-x}Se_x$  based solar cells were fabricated on fluorine doped tin oxide (FTO) substrate using cadmium sulfide (CdS) as a window layer. The CdS layer was

deposited onto cleaned FTO coated glass by a chemical bath deposition technique, where solution containing cadmium chloride  $CdCl_2$  (5 ml), triethanolamine (TEA) (2.5 ml), ammonium hydroxide (5 ml), thiourea (5 ml) and preheated deionized water (32.5 ml). The bath was kept at 70 °C for 20 minutes [124]. The chemical reaction involving the formation of CdS can be explained as follows.

$$Cd^{2+} + 4NH_3 \rightleftharpoons [Cd(NH_3)_4]^{2+}$$
<sup>(1)</sup>

$$CS(NH_2)_2 + OH^- \rightleftharpoons HS^{-1} + H_2O$$
<sup>(2)</sup>

$$\mathrm{HS}^{-1} + \mathrm{OH}^{-} \rightarrow \mathrm{S}^{2-} + \mathrm{H}_{2}\mathrm{O} \tag{3}$$

$$Cd^{2+} + S^{2-} \rightarrow CdS \tag{4}$$

 $Cd^{2+}$  are slowly released from the amino complexes of cadmium, which then react with  $S^{2-}$  ions formed by the alkaline hydrolysis of thiourea [125].

The as prepared CdS film was heated in an air furnace at 400 °C for 1 hour. After CdS deposition, the absorber layer (AgSbS<sub>2</sub> and AgSbS<sub>2-x</sub>Se<sub>x</sub>) was deposited as mentioned in sections 3.2 and 3.3. Using silver paint, an electrode with 0.10 cm<sup>2</sup> area was painted (SPI supplies) to form an ohmic contact. The image below provides a schematic illustration of the photovoltaic device.



Figure 3.7 Schematic representation of Solar cells: glass/FTO/AgSbS<sub>2-x</sub>Se<sub>x</sub>/CdS/C/Ag.

#### **3.6.2 Photodetectors**

Photodetectors in photoconductive and photodiode modes were fabricated. In photoconductive mode, the thin films were deposited on glass substrate and then a pair of Ag electrodes of equal dimensions were painted. In the photodiode, n type CdS layer was deposited on FTO, followed by p-type AgSbS<sub>2-x</sub>Se<sub>x</sub>. Two metal contacts were taken, one

from the surface and the other from the FTO. The photodetectors were illuminated with different LEDs of power 20 W and lasers of wavelength 405, 532, 785, 842 and 1064 nm.

# **3.7 Characterization**

# 3.7.1 X-ray diffraction (XRD)

In this work we used the X-ray diffraction technique for the crystal structure analysis of different compounds. XRD analysis were done in normal mode as well as grazing incidence (GIXRD). A PANalytical (Empyrean) diffractometer employing Cu-K $\alpha_1$  source ( $\lambda$  = 1.54056 Å) was employed for recording the XRD patterns. The experimental data were compared with the standard JCPDS data to determine the crystal structure.

Further from the respective XRD patterns the average crystallite size (D) and microstrain ( $\epsilon$ ) of the films can be calculated using the Williamson-Hall (W-H) plot [108].

$$\beta Cos\theta = 4\varepsilon Sin\theta + k\lambda/D \tag{5}$$

W-H plot of  $\beta$ Cos $\theta$  vs Sin $\theta$ , is a straight line plot, in which the slope contains  $\varepsilon$  and the intercept is related to the crystallite size, where  $\beta$  is the full width at half maximum (FWHM) of the prominent peaks at 2 $\theta$ , 'D' is the average crystallite size, ' $\lambda$ ' is the X-ray wavelength (1.54056 Å),  $\theta$  is the angle of diffraction and K is the shape factor (~ .90).

# 3.7.2 Raman spectroscopy

Raman spectroscopy is a technique used for the analysis of phase, and molecular interactions. This technique is based on the Raman effect, which occurs due to inelastic scattering of light. Most of the photons that interact with a crystal are scattered elastically; a small amount of light is scattered inelastically at a frequency different from the initial photon. The process of inelastic scattering is termed as Raman effect [126].

Raman spectral studies were carried out using a Thermo scientific DXR Raman microscope employed with a 532 nm laser. The spectra were collected from wavenumbers ranging 50 to  $300 \text{ cm}^{-1}$ .

# **3.7.3 X-ray Photoelectron spectroscopy (XPS)**

XPS is a surface analysis method used to determine a material's chemical state and elemental composition. This spectroscopic technique is based on Photoelectric effect. Soft X-rays (Mg K or Al K) are used in this approach to irradiate the surface. Through their interactions with the surface atoms, these photons cause the photoelectric effect, which

releases electrons. The electrons are emitted with certain kinetic energy, given by the equation,

$$KE = h\nu - BE - \Phi s \tag{6}$$

Where hv is the energy of X-ray photons used (photon energy), BE is the energy of an electron attracted to a nucleus (binding energy) and  $\Phi s$  is the spectrometer work function [127]. The work function and photon energy are known, kinetic energy value is measured by the detector, so the binding energy can be calculated from the equation. In XPS binding energy is plotted against number of photoelectrons emitted. Peaks in an XPS spectrum are caused by photoelectrons emitting from the core levels of the element. The binding energy of core electrons also depends upon the chemical environment of the atom, known as chemical shift. The bonding structure can be determined from the chemical shift [128].

In this work chemical states and elemental composition of the compounds were analyzed using Thermo Scientific K-alpha X-ray photoelectron spectrometer with monochromatic Al K- $\alpha$  radiation of energy 1486.6 eV. For all the XPS peaks BE corrections were done using adventitious carbon (C 1s, 284.60 eV). Deconvolution of the peaks was done by applying Shirley type background and peak fitting by sum of the Gaussian -Lorentzian function.

# **3.7.4 Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX)**

SEM is used to determine the surface morphology. In SEM a high energy electron source or an electron gun emits electrons that are accelerated by an applied voltage, and as a result of the high energy electron beam's interaction with the specimen, secondary electrons, back scattered electrons (BSE), and distinctive X-rays are produced [129]. The secondary and BSE are mainly used for imaging the sample surface. The morphology and topography of the samples are produced by secondary electrons. In many materials the mean free path length of secondary electrons is 10Å, so in comparison with BSE and X-rays the volume of production of secondary electrons is small. Hence, the secondary electrons are perfect for examining the topography [130].

The elemental composition of the material imaged in SEM is detected by EDX. Electrons are ejected from the atoms on the sample surface when the electron beam strikes

33

it. To balance the energy between the two electrons, the void left behind by the ejection of an electron is filled with a second electron from a higher shell, which causes X-ray emission. The element can be detected from the characteristics X-ray produced. The detector counts the X-rays and calculates their respective energies [131]. In this work morphology of the samples was examined by field emission scanning electron microscopy (FESEM, Hitachi SU 8020).

#### **3.7.5** Transmission electron microscopy (TEM)

The transmission electron microscope is an imaging technique used for the characterization of nanometer scale materials. A monochromatic beam of electrons is accelerated through the high potential (100 to 300 kV). These accelerated electrons are then passed through electromagnetic lenses, which focus the electrons into a very fine beam [132]. TEM provides topographical, morphological, crystalline and compositional information. We used TEM (FEI Titan G2 80-300) for morphology and crystal structure analysis. The TEM samples were prepared on Cu coated carbon grids. A small drop of nanocolloid was dried on the grid at ambient temperature.

### **3.7.6** Atomic force microscopy (AFM)

The Atomic Force Microscope is used to analyze and characterize samples at the microscope level. This technique provides a field view ranging from atomic and molecular scales and above 125  $\mu$ m. The main advantage of using AFM over electron microscopes is, it can provide 3D images of the surface [133]. Atomic force microscopy (AFM) (NT-MDT Solver pro) in contact mode was used to analyze the surface topography of the thin films.

# **3.7.7 UV-Vis-NIR spectroscopy**

UV-Vis-NIR spectrometers measure light intensity at a certain wavelength to determine a material's transmission or reflection and thereby absorption. The absorption coefficient of the material can be calculated from the equation given below [100].

$$\alpha = \frac{1}{d} \ln \left[ \frac{(1-R)^2}{T} \right]$$
(7)

Where  $\alpha$  is the absorption coefficient, T is the transmittance, R is the reflectance and d is the average thickness of the thin film (cm). The average thickness of the film was measured using the profilometer technique. From the absorption coefficient the energy bandgap can be calculated from the equation given below.

$$(\alpha h\nu)^n = A(h\nu - E_g) \tag{8}$$

Here A is a constant, v is the frequency and  $E_g$  is the optical bandgap. For an optical transition, the value of n changes; it is 2, 1/2 and 2/3 for direct allowed, indirect allowed, and direct forbidden transitions, respectively. The bandgap was determined by extrapolating  $(\alpha hv)^n$  vs (hv) plot (Tauc plot) on the x axis, where  $(\alpha hv)^n = 0$  gives the optical bandgap. In this work the optical transmittance, reflectance and absorbance of the films was recorded using UV-Vis-NIR spectrophotometer (JASCO-V770). The thin film was placed in the sample holder with a reference substrate (plain glass). Two glass substrates were used for the baseline measurement, one in the reference path and the other in the sample path, and the entire area was scanned.

#### 3.7.8 Electrical characterization

The electrical properties of the thin films and the devices were examined by measuring the photocurrent response. Electrical contacts of 7 mm in length separated by 7 mm were painted using silver paints (SPI supplies). The electrical measurements were performed using a computer interfaced Keithley 6487 picoammeter/voltage source. The measurements were done using a tungsten lamp (50 W), LEDs of different wavelengths, 532 and 785 nm continuous lasers with varying power densities and 405 and 840 nm diode lasers and 1064 nm laser. The measurements were done in both dark and illumination conditions at an interval of 20 seconds.

The electrical properties such as carrier concentration, carrier mobility and resistivity of the samples were measured using a Hall effect measurement system (Ecopia HMS-3000) equipped with a 0.5 T magnet. For the measurements, 4 electrical contacts were painted at the corners of the sample placed on SPCB-1 spring clip board. The spring-loaded tips were made in contact with the sample through the silver contact. The spring clip board along with sample was placed inside the sample measurement case. The measurements were done at room temperature by applying a magnetic flux density of 0.5 T.

# 3.7.9 J-V measurements

The characterization of solar cells was done by measuring the I-V measurements using a Keithley 6487 pico ammeter/voltage source. On the x and y axes, the measured voltage and current density (current per unit area) were plotted. Open circuit voltage ( $V_{oc}$ ) is represented by the intersection at the x axis where the current is zero, while short circuit current is represented by the intersection at the y axis when the voltage is zero ( $I_{sc}$ ). The back

contact was made using silver paint and a front contact from the FTO. During the voltage sweep, voltage and current were monitored using these top and bottom electrodes. The PV structures were illuminated using an Oriel solar simulator with AM 1.5 radiation at an intensity of 1000  $W/m^2$ .

The efficiency  $(\eta)$  of the solar cells can be calculated using the equation given below

$$\eta = \frac{P_{MP}}{P_{in}} = \frac{V_{oc}I_{sc} FF}{P_{in}}$$
(9)

where  $P_{MP}$  is the maximum power,  $P_{MP} = V_{MP} I_{MP}$ , which is the area of the largest rectangle on the I-V curve.  $P_{in}$  is the incident power. The fill factor FF is the measure of the squareness of I-V curve and always less than 1.

$$FF = \frac{V_{MP}I_{MP}}{V_{oc}I_{sc}} \tag{10}$$

AgSbS<sub>2</sub> and AgSbS<sub>2-x</sub>Se<sub>x</sub> thin films were prepared by combining chemical bath deposition, thermal evaporation and spin coating techniques. Various characterization techniques such as XRD, XPS, Raman spectroscopy, SEM, TEM, AFM, UV-Vis-NIR spectroscopy and photoresponse measurements were used for the analysis of various properties of these films. Further, thin films synthesized at different conditions were used in solar cells and photodetector applications. The properties of the fabricated devices were also studied using different techniques.

The complete study on  $AgSbS_2$  thin films and its application in photovoltaic device will be discussed in the next chapter.

# **CHAPTER 4**

# AgSbS<sub>2</sub> THIN FILMS FOR PHOTOVOLTAIC APPLICATIONS

This chapter discusses the formation of monoclinic AgSbS<sub>2</sub> thin films and their incorporation in solar cells with a device structure FTO/n-CdS/p-AgSbS<sub>2</sub>/C/Ag.

The synthesis of  $AgSbS_2$  thin films involves the thermal treatment of precursors layers of Ag thermally evaporated over  $Sb_2S_3$ . The chemical reaction involving the formation of  $Sb_2S_3$  from the chemical bath containing  $SbCl_3$  and  $Na_2S_2O_3$  is explained below, Initially  $SbCl_3$  react with  $Na_2S_2O_3$  to form  $(Sb_2(S_2O_3)_3)$ 

$$2SbCl_3 + 3Na_2S_2O_3 \rightarrow Sb_2(S_2O_3)_3 + 6NaCl$$
(11)

Next  $(Sb_2(S_2O_3)_3)$  is hydrolyzed to form  $Sb_2S_3$ , the corresponding reaction is given below.

$$Sb_2(S_2O_3)_3 + 6H_2O \rightarrow Sb_2S_3 + 3HSO_4^- + 3H_3O^+$$
 (12)

The photographs of precursor layers and AgSbS<sub>2</sub> thin films are presented in Figure 4.1.



Figure 4.1 Photographs of Sb<sub>2</sub>S<sub>3</sub>, Sb<sub>2</sub>S<sub>3</sub>-Ag and AgSbS<sub>2</sub> thin films on glass.

# 4.2 Results and discussions

# 4.2.1 Structure

Diffraction patterns of as prepared and heated  $Sb_2S_3$ , as prepared and heated glass/Sb<sub>2</sub>S<sub>3</sub>-Ag samples with silver thicknesses 5, 10 and 20 nm are presented in Figure 4.2a. The as prepared Sb<sub>2</sub>S<sub>3</sub> is amorphous and upon heating at 350 °C for 30 minutes, the film turns to orthorhombic form (Sb<sub>2</sub>S<sub>3</sub>(PDF#42-1393)) represented by the planes marked as (020), (120), (220), (310), (021), (221), (240), (520) and (501). For samples 5 and 10 nm the samples formed after heating show peaks corresponding to the orthorhombic Sb<sub>2</sub>S<sub>3</sub>, even though the

intensity reduces as Ag content increases. For 20 nm Ag sample,  $Sb_2S_3$  peaks almost disappear, and two new peaks identified as (400) and ( $\overline{3}12$ ) planes originate due to the commencement of the crystallization of AgSbS<sub>2</sub> as seen in the figure. No reflections due to Ag are present in these samples.

The XRD patterns of glass/Sb<sub>2</sub>S<sub>3</sub>-Ag films with a varying silver thickness (50, 60, 80 100, and 110 nm) before and after annealing at 350 °C for 30 min are displayed in Figure 4.2.b-c. For the as deposited glass/Sb<sub>2</sub>S<sub>3</sub>-Ag films, the diffraction peaks located at  $2\theta$  = 38.23°, 44.36°, 64.51° correspond to (111), (200), (220) planes of face centered cubic silver (PDF#04-0783) and no peaks of Sb<sub>2</sub>S<sub>3</sub> due amorphous nature of the chemically deposited as mentioned above. As seen in Figure 4.2(c), after heating the Ag peaks vanish and new peaks begin to present at  $2\theta = 27.65^{\circ}$ ,  $31.58^{\circ}$ , and  $39.61^{\circ}$  which are indexed by (400), ( $\overline{3}12$ ) and  $(\overline{1}15)$  planes of monoclinic AgSbS<sub>2</sub> (PDF#72-1095). From the figure, for all the samples with different Ag thicknesses 50-110 nm, the diffraction peaks at  $2\theta = 27.65^{\circ}$ ,  $31.58^{\circ}$  and  $39.61^{\circ}$ match with the standard monoclinic AgSbS<sub>2</sub> (PDF# 72-1095) corresponding to the planes (400),  $(\overline{3}12)$  and  $(\overline{1}15)$  (marked as square). Peak intensities that differ from the standard values suggest that the film growth is oriented those planes perpendicular to the substrate surface. This type of crystallite growth along distinct planes was also reported for monoclinic AbSbS<sub>2</sub> thin films grown by chemically deposited  $Sb_2S_3$  thin films dipped in silver nitrate solution [95]. Also, in the figure we can see that as silver thickness increases (400) and  $(\overline{1}15)$ , planes grow stronger. Further, all the samples show a peak at  $2\theta = 34.53^{\circ}$ , slightly shifted from the standard AgSbS<sub>2</sub> peak. This can be attributed to the presence of Ag<sub>3</sub>SbS<sub>3</sub> (PDF# 87-0709, denoted as a star) phase in the films, and as observed in the figure, the peak intensity increases with Ag thickness.



Figure 4.2 a) XRD of as prepared and heated  $Sb_2S_3$  and heated  $Sb_2S_3$ -Ag thin films with varying silver thickness (Ag = 5, 10, and 20 nm), b)  $Sb_2S_3/Ag$ , with silver thickness as 50, 60, 80, 100, and 110 nm (a) as prepared (b) thin films heated at 350 °C, 30 minutes in vacuum. Reproduced with kind permission from Elsevier [108].

The XRD plot was used to calculate the crystallite size, microstrain, and dislocation density of each sample. The crystallite size and microstrain are calculated using the Williamson-Hall (W-H) plot, given in Figure 4.3.





Figure 4.3 W-H plot of AgSbS50, AgSbS60, AgSbS80, AgSbS100 and AgSbS110 thin films. Reproduced with kind permission from Elsevier [108].

Then, the dislocation density ( $\delta$ ) for the samples was calculated using the equation,

$$\delta = \frac{1}{D^2} \tag{13}$$

The calculated microstrain, dislocation density and crystallite size values are tabulated below in Table 4.1. From the table, we can observe that the microstrain and dislocation density increase as crystallite size decreases, implying an increase in the lattice imperfections. Table 4.1 Microstrain, dislocation density and crystallite size of the thin films. Reproduced with kind permission from Elsevier [108].

Sample	Microstrain (ε)	Dislocation density	Crystallite size
		(nm <sup>-2</sup> ) ×10 <sup>-4</sup>	( <b>nm</b> )
AgSbS50	2×10 <sup>-4</sup>	2.2	68
AgSbS60	5.8×10 <sup>-4</sup>	2.4	64
AgSbS80	3.4×10 <sup>-3</sup>	4	50
AgSb100	10×10 <sup>-2</sup>	4.9	45
AgSb110	80×10 <sup>-2</sup>	5.6	42

A crystal structure analysis of the AgSbS50 sample was also performed using highresolution TEM (HRTEM). From the HRTEM analysis given in Figure 4.4, interplanar spacings of 3.15, 4.03 and 2.20 Å corresponding to (400), ( $\overline{1}11$ ) and ( $\overline{1}15$ ) planes of monoclinic AgSbS<sub>2</sub>. All these analyses confirm the formation of monoclinic AgSbS<sub>2</sub> as the major phase.



Figure 4.4 High resolution TEM image of AgSbS50 sample. Reproduced with kind permission from Elsevier [108].

# 4.2.2 Composition

The composition of the elements and their chemical states in the samples are determined using the XPS, spectra were recorded after surface etching by argon ion. The binding energy was corrected by adventitious carbon peak at 284.6 eV, in addition to the charge compensation by the flood gun equipped with the system [123]. The high-resolution core level spectra of as prepared and heated samples were analyzed.

Figure 4.5 shows the survey spectrum of AgSbS100 sample. The spectrum displays the presence of C, Ag, Sb and S on the film surface. The presence of C is due to the adventitious carbon.



Figure 4.5 XPS survey spectrum of AgSbS100 sample.

Figure 4.6 (a-c) represents the high resolution XPS spectra of Ag 3d, Sb 3d, and S 2p for the as prepared glass/Sb<sub>2</sub>S<sub>3</sub>-Ag precursor layer with Ag = 100 nm. Ag 3d region consists of spin-orbit coupled  $3d_{5/2}$  and  $3d_{3/2}$  peaks at 368.34 and 374.34 eV separated by 6 eV ( $\Delta$ E) and the doublet binding energy values correspond to the metallic silver (Ag<sup>0</sup> state). The two satellite peaks (marked in circles) are loss peaks caused by core electron interactions with free electrons in silver metal [127]. As shown in Figure 4.6b, the Sb 3d spectrum is deconvoluted into two doublets pairs composed of Sb  $3d_{5/2}$  and Sb  $3d_{3/2}$  singlets. The first one is compatible with the Sb<sup>3+</sup> state in Sb<sub>2</sub>S<sub>3</sub> with binding energies of 530.58 and 539.92 eV, separated by 9.34 eV. The minor peaks (I and II) marked as Sb  $3d_{5/2}$  (529.21 eV) and Sb  $3d_{3/2}$  (538.32 eV)are attributed to the metallic state of Sb (Sb<sup>0</sup>), which is typical in Sb-based compounds as a result of the sputtering effect during the etching process [77]. The S  $2p_{3/2}$  and S  $2p_{1/2}$  peaks are at 161.90 and 163.11 eV with  $\Delta$ E of 1.21 eV coinciding with that of S<sup>2-</sup> state in Sb<sub>2</sub>S<sub>3</sub> [134].



Figure 4.6 XPS high resolution core level spectra of (a) Ag3d, (b) Sb3d, and (c) S2p of glass/Sb<sub>2</sub>S<sub>3</sub>-Ag precursor layer. Reproduced with kind permission from Elsevier [108].

The core level spectra of Ag 3d, Sb 3d and S 2p in AgSbS100 are presented in Figure 4.7(a-c). From Figure 4.6a, Ag  $3d_{5/2}$  and  $3d_{3/2}$  at B.E values of 368.2 and 374.2 eV imply Ag<sup>+</sup> state in AgSbS<sub>2</sub> as reported in previous studies [91,135]. Figure 4.7b shows Sb  $3d_{5/2}$  and Sb  $3d_{3/2}$  peaks .The major peaks at 530 eV and 539.34 eV are due to Sb<sup>3+</sup> originated from AgSbS<sub>2</sub> [97] and the minor ones (I and II) are assigned to a metallic peak of Sb  $3d_{5/2}$  (528.14 eV) and Sb  $3d_{3/2}$  (537.30 eV). Figure 4.7c displays S 2p spectrum deconvoluted to S  $2p_{3/2}$  and S  $2p_{1/2}$  doublet pair with the respective peaks located at 161.35 eV and 162.56 eV, indicating S<sup>2-</sup> state in AgSbS<sub>2</sub> [91,135,136].


Figure 4.7 XPS high resolution spectra of the core levels of (a) Ag 3d, (b) Sb 3d, and (c)S 2p of AgSbS100. Reproduced with kind permission from Elsevier [108].

Further, the depth profile analysis of the as synthesized glass/Sb<sub>2</sub>S<sub>3</sub>-Ag and AgSbS100 films is given in Figure 4.8a-b. The as synthesized precursor depth profile shows that the surface is composed of dominantly Ag signals; Sb and S signals are noisy. The depth profile of AgSbS100 exposes that the elements Ag, Sb and S are distributed uniformly throughout the depth, from the surface to substrate. In this case, along with Sb 3d peaks O1s peaks are also observed at the surface as well as at glass-substrate interface. Si signal begins simultaneously at the film, the glass substrate-film interface.



Figure 4.8 Depth profile analysis of a) glass/Sb<sub>2</sub>S<sub>3</sub>-Ag b) AgSbS100. Reproduced with kind permission from Elsevier [108].

### 4.2.3 Morphology

Figure 4.9 a-h shows SEM images of as-prepared glass/Sb<sub>2</sub>S<sub>3</sub>-Ag with Ag thicknesses of 50, 100, and 110 nm, as well as AgSbS50, AgSbS100, and AgSbS110. As seen in the figure (Figure 4.9a, c and d) the precursor samples show a compact morphology with uniformly distributed small grains of size in the range of 44-55 nm. The surface morphology of the AgSbS<sub>2</sub> films (AgSbS50, AgSbS100 and AgSbS110) is shown in Figures 4.9b, d and e. Bigger grains that are spherical and interconnected are observed in AgSbS<sub>2</sub> films [91,94]. The increased particle size (80-90 nm) in AgSbS<sub>2</sub> films indicates that annealing caused recrystallization and increased grain growth [97]. AgSbS60 and AgSbS80 sample SEM images are shown in Figure 4.9g, h. Both samples exhibit smaller grains compared to AgSbS50 sample.



Figure 4.9 Scanning electron micrographs of AgSbS<sub>2</sub> thin films (a) AgSbS50 (c) AgSbSbS100 (e) AgSbS110 as deposited and (b) AgSbS50 (d) AgSbS100 (f) AgSbS110 (g)

AgSbS60 (h) AgSbS80 annealed at 350 °C for 30 minutes in vacuum. Reproduced with kind permission from Elsevier [108].

The surface topography of the samples was analyzed using atomic force microscopy in contact mode. The images were recorded by scanning the sample surface area of  $2 \ \mu m \times 2 \ \mu m$ . Figure 4.10 (a, b), (c, d) and (e, f) shows 2D and 3D topography images of AgSbS50, AgSbS100 and AgSbS110 samples. From the figure the samples are composed of spherical particles. Uniformly distributed spherical particles are observed in AgSbS50 sample. The average roughness values of the films were 11, 14 and 22 nm respectively for AgSbS50, AgSbS100 and AgSbS110 samples. As the Ag thickness increases the roughness also increases. Figure 4.11a, b, and c represent the contact error images of AgSbS50, AgSbS100 and AgSbS110.







Figure 4.10 Atomic force micrographs of (2D) (a) AgSbS50, (c) AgSbS100, (d) AgSbS110 and (b, e, and f) their corresponding 3D images. Reproduced with kind permission from Elsevier [108].



Figure 4.11 Contact error images of (a) AgSbS50, (b) AgSbS100 and (c) AgSbS110 samples. Reproduced with kind permission from Elsevier [108].

The elemental composition and the mapping for AgSbS50 sample were analyzed using SEM-EDX mapping. Figure 4.12 presents EDX elemental mapping and area scans. Ag, Sb, S elements are detected in the sample as noted in the figure.



Figure 4.12 EDX mapping of AgSbS50 sample.

### **4.2.4 Optical properties**

The absorbance, transmittance, and reflectance spectra of AgSbS<sub>2</sub> thin films with different thickness were measured using UV-Vis-NIR spectroscopy in the wavelength range of 400-1600 nm. The absorption spectra, transmittance, reflectance and Tauc plots are illustrated in Figure 4.13. The films show good absorption in the visible region that begin around 600-800 nm range. The thicknesses of the films were measured using profilometer, and the values are 235, 245, 265,285 and 295 nm for AgSbS50, AgSbS60, AgSbS80, AgSbS100 and AgSbS110 respectively.

The bandgap values were calculated from transmittance and reflectance spectra. The equation used for the bandgap calculation is given below [137].

$$(\alpha h\nu)^2 = A(h\nu - E_g) \tag{14}$$

For this, the Tauc plot  $(\alpha h\nu)^2$  vs.  $h\nu$  corresponding to direct transition is drawn. Bandgap is obtained from the Tauc plot, by extrapolating the linear portion span to  $h\nu$  axis. Calculated bandgap values for AgSbS<sub>2</sub> films are 1.70 eV (AgSbS50), 1.71 eV (AgSbS60), 1.73 eV (AgSbS80), 1.74 eV (AgSbS100) and 1.78 eV (AgSbS110) and the values are correlated with the direct bandgap reported for monoclinic AgSbS<sub>2</sub> [92,95]. The optical bandgap value decreases as silver thickness increases, which could be due to the size confinement effect. Bandgap tailoring at higher silver thicknesses may be caused by higher dislocation density and microstrain values. These band gap values are close to the ideal bandgap for photovoltaic applications.



Figure 4.13 a) Absorbance spectra b) transmittance and reflectance spectra c) Tauc plots of AgSbS50, AgSbS60, AgSbS80, AgSbS100 and AgSbS110 thin films. Reproduced with kind permission from Elsevier [108].

The observed experimental bandgap values are well in agreement with the theoretical calculations. Even though the electronic calculations showed an indirect nature, the band structure displays direct allowed transitions corresponding to similar energies closer to the  $\Gamma$ - point.

### **4.2.5 Electrical properties**

Figure 4.14 a-d depicts the photocurrent response results recorded steadily in an interval of 20 s in the dark, under illumination by 50 W halogen lamp, and after off the illumination, at a bias voltage of 0.5 V. Contacts were taken from two silver electrodes of the same dimension. The photocurrent of AgSbS10, AgSbS20 and AgSbS50 samples is in the order of  $10^{-11}$  A. From the bias voltage, photocurrent, and thickness of the films, the conductivity of the samples were calculated, the values are  $0.34 \times 10^{-5}$  ( $\Omega$  cm)<sup>-1</sup>,  $0.65 \times 10^{-4}$  ( $\Omega$  cm)<sup>-1</sup> and  $6 \times 10^{-3}$  ( $\Omega$  cm)<sup>-1</sup> for AgSbS10, AgSbS20 and AgSbS50 respectively. The sulfide samples with 100 and 110 nm Ag contents showed metallic conductivity in the order of  $10^2$  ( $\Omega$  cm)<sup>-1</sup> and hence no photoresponse. Cyclic photocurrent response measurements were also done for AgSS10, AgSbS20 and AgSbS50 samples, presented in Figure 4.14d. The five cycle photoresponse shows a constant value of rise and decays current which indicates that the sample is stable under dark light conditions.





Figure 4.14 Photoresponse curve of heated  $Sb_2S_3/Ag$  films with silver thickness a) 10 nm b) 20 nm and c) 50 nm, cyclic photoresponse of d)10, 20, and 50nm. Reproduced with kind permission from Elsevier [108].

Further, the photosensitivity of the films were calculated using the equation given below [92].

$$S(\%) = \frac{I_{light} - I_{dark}}{I_{dark}} \times 100$$
(15)

Where S corresponds to sensitivity,  $I_{light}$  and  $I_{dark}$  indicate the current generated in the light and dark conditions. And also the respective conductivity values by four probe method. The values of sensitivity are 20, 23 and 46% for AgSbS10, AgSb20 and AgSS50 respectively. As the silver thickness increases sensitivity also increases, this can be due to larger grains in AgSbS50 as observed from the XRD analysis.

The Hall coefficient, carrier mobility and carrier concentration were measured using a Hall effect measurement system. The measured values AgSbS50, AgSbS60, AgSbS80, AgSbS100 and AgSbS110 films are given in the table below. Due to the highly resistive nature of AgSbS10 and AgSbS20 films, the measurements resulted in inconsistent values. Table 4.2 Hall coefficient, carrier concentration, hall mobility and conductivity values of AgSS50, AgSbS60, AgSbS80, AgSbS100 and AgSbS110 thin films. Reproduced with kind permission from Elsevier [108].

Sample	Hall	Carrier	Carrier Hall	
	coefficient	concentration	Mobility	(Ωcm) <sup>-1</sup>
	(RH, cm <sup>3</sup> /C)	( <b>cm</b> <sup>-3</sup> )	(cm <sup>2</sup> /V.s)	
AgSbS50	6.8×10 <sup>4</sup>	9.1×10 <sup>13</sup>	6.7	1×10 <sup>-4</sup>
AgSbS60	3×10 <sup>3</sup>	5×10 <sup>15</sup>	$1.1 \times 10^{3}$	3.3×10 <sup>-1</sup>
AgSbS80	$2 \times 10^{2}$	2×10 <sup>16</sup>	$2.6 \times 10^3$	1.1×10 <sup>-1</sup>
AgSbS100	$1.0 \times 10^{2}$	5.9×10 <sup>16</sup>	$1.7 \times 10^{4}$	$1.66 \times 10^2$
AgSbS110	6.2	$1.0 \times 10^{18}$	$2.0 \times 10^{3}$	$3.35 \times 10^{2}$

The positive Hall coefficient value confirms the p-type conductivity of the samples. The carrier mobility and carrier concentration increase with Ag thickness. The measured conductivity values are in correlation with the conductivity measured from the photoresponse measurements.

### 4.2.6 Photovoltaic device

The solar cells were made using AgSbS<sub>2</sub> formed at different conditions as the absorber layer and CdS as the window layer. The device structure can be written as FTO/n-CdS/p-AgSbS<sub>2</sub>/C/Ag. AgSbS10, AgSbS20, AgSbS50, AgSbS60 and AgSbS80 samples were incorporated in solar cells as the absorber layer. The active area of the solar cell was 0.1 cm<sup>2</sup>. The schematic diagram of the fabricated solar cell structure is given in Figure 4.15.



Figure 4.15 Schematic of glass/FTO/n-CdS/p-AgSbS<sub>2</sub>/C/Ag solar cell.

The J-V characteristics of solar cells are given Figure 4.16.a-b. The dark characteristics of the cell show good diode rectification behavior as evident in the figure. The solar cells fabricated with  $AgSbS_2$  of 10 and 20 nm silver thickness present poor photovoltaic parameters (Figure 4.16a). Low value of V<sub>oc</sub> and J<sub>sc</sub> is observed for cell with AgSbS<sub>2</sub> of 10 nm Ag. An improvement in the  $V_{oc}$  and  $J_{sc}$  is observed for Ag = 20 nm solar cell, therefore the efficiency increased from 0.1 to 0.3%. The evaluated photovoltaic parameters are presented in Table 3. The J-V curves of AgSbS50 solar cells under illumination presents V<sub>oc</sub> = 530 mV,  $J_{sc}$  = 5.5 mA/cm<sup>2</sup>, fill factor (FF) = 0.50, and the calculated efficiency = 1.5 %, slightly higher value of efficiency compared to that reported solar cell efficiency [94,98] with significantly higher values of Voc and FF values. For AgSbS50 solar cells, the efficiency increased 5 times and J<sub>sc</sub> increased 4 times compared to the 20 nm sample based solar cell. The improved efficiency of AgSbS50 based solar cells is due to better crystallinity, bigger grain size and higher conductivity compared to other films. The series and shunt resistance values are 32 and 475  $\Omega$  cm<sup>2</sup>, evaluated from the inverse of slope at V<sub>oc</sub> and J<sub>sc</sub> respectively. The AgSbS60 and AgSbS80 were also incorporated in the solar cells. Due to the high conductivity and metallic behavior of these samples, the solar cell performance is poor as presented in Figure 4.16b.



Figure 4.16 J-V characteristics of (a) glass/FTO/n-CdS/p-AgSbS<sub>2</sub>/carbon/silver structure in which Ag thickness is a) 10, 20 and 50 nm b) 60 and 80 nm. Reproduced with kind permission from Elsevier [108].

The formation of  $AgSbS_2$  ternary can be explained based on the interlayer diffusion controlled by solid state reaction described by previous reports of other compounds [138– 140]. In this case first, ~185 nm Sb<sub>2</sub>S<sub>3</sub> precursor film is formed by the chemical reaction between Sb<sup>3+</sup> and S<sup>2-</sup> followed by the nucleation and film growth on the substate surface [95]. The minimum Ag thickness required for the formation of AgSbS<sub>2</sub> is 26 nm calculated from the density and formula mass values of the materials. High density defects, disorders and changes in atomic arrangements due to Ag diffusion are key factors leading to the formation of ternary AgSbS<sub>2</sub> due to inter layer diffusion and chemical reaction.

Based on all the findings described in this chapter, we can conclude that the structural, morphological, opto-electric properties of AgSbS<sub>2</sub> thin films synthesized by heating glass/Sb<sub>2</sub>S<sub>3</sub>-Ag precursor layers were strongly dependent upon the Ag layer thickness in the film. The photovoltaic device made with AgSbS<sub>2</sub> absorber and CdS window layer demonstrated good PCE with photovoltaic parameters,  $V_{oc} = 530 \text{ mV}$ ,  $J_{sc} = 5.5 \text{ mA/cm}^2$ , FF = 0.50, and an efficiency 1.5%, the highest values ever recorded for glass/FTO/n-CdS/p-AgSbS<sub>2</sub>/C/Ag based p-n junction solar cell.

The analysis of  $AgSbS_{2-x}Se_x$  thin films and its applications in solar cells and photodetectors will be discussed in the next chapter.

# **CHAPTER 5**

## AgSbS<sub>2-x</sub>Se<sub>x</sub> THIN FILMS WITH VARYING COMPOSITION: CHARACTERIZATION AND DEVICE FABRICATION

This chapter describes a systematic study on changes in structure, morphology, composition and opto-electronic properties of the  $AgSbS_{2-x}Se_x$  films with varying composition formed by partial substitution of sulfur with selenium via heating glass/Sb<sub>2</sub>S<sub>3</sub>-Ag<sub>2</sub>Se precursor layers formed by dipping glass/Sb<sub>2</sub>S<sub>3</sub>-Ag in sodium selenosulfate solution. Moreover, the performance of  $AgSbS_{2-x}Se_x$  based solar cell as well as photodetector are also described here.

### 5.1 Results and discussions

### 5.1.1 Crystal structure: Effect of Ag thickness and selenization time

The photographs of the precursor layers and  $AgSbS_{2-x}Se_x$  thin films are presented in Figure 5.1.



Figure 5.1 Photographs of precursor layers and AgSbS<sub>2-x</sub>Se<sub>x</sub> thin films.

AgSbSe<sub>2-x</sub>Se<sub>x</sub> thin films with different Ag thickness were synthesized. The diffraction patterns of heated glass/Sb<sub>2</sub>S<sub>3</sub>-Ag<sub>2</sub>Se with Ag thickness 10, 20, 40, 60 and 80 nm are given in Figure 5.2. For sample with Ag thickness 10 nm, peaks located at  $2\theta = 15.72^{\circ}$ , 17.47°, 24.92°, 29.20, 32.30 are assigned to orthorhombic Sb<sub>2</sub>S<sub>3</sub> (PDF#06-0474), corresponding planes are (020), (120), (130), (021) and (221). For 20 nm silver thickness additional peaks originate at 27.13°, 31.37° and 45.19° which can be due to the beginning of crystallization to form the ternary.

As the silver thickness increases, three peaks are detected at 27.08°, 31.48° and 45.08°. These peaks were compared with that of cubic AgSbS<sub>2</sub> and AgSbSe<sub>2</sub>. The shift from both these compounds indicates the formation of the solid solution of AgSbS<sub>2-x</sub>Se<sub>x</sub>. The normalized (200) peak is given in Figure 5.2b. The calculated average crystallite size values are 12, 23 and 18 nm for AgSbS<sub>2-x</sub>Se<sub>x</sub> with 40, 60 and 80 nm Ag thickness, respectively. The x value for the samples was calculated using Vegard's law [141]. According to the law, lattice parameter 'a' of the solid solution can be related to that of the respective pure compounds as  $a_{AgSb(S_{1-x}Se_X)_2} = (1 - X)a_{AgSbS_2} + (X)a_{AgSbSe_2}$ , where a is the respective lattice parameter. The calculated x values are 0.34, 0.60 and 0.56 and the corresponding composition AgSbS<sub>1.66</sub>Se<sub>0.34</sub>, AgSbS<sub>1.40</sub>Se<sub>0.60</sub> and AgSbS<sub>1.44</sub>Se<sub>0.56</sub> for 40, 60 and 80 nm films respectively.



Figure 5.2 a) XRD patterns of heated glass/Sb<sub>2</sub>S<sub>3-</sub>Ag<sub>2</sub>Se films with silver thickness 10, 20, 40, 60 and 80 nm b) normalized (200) peak. Reproduced with kind permission from Elsevier [109].

XRD patterns of samples formed by heating selenized glass/Sb<sub>2</sub>S<sub>3</sub>-Ag precursors are analyzed as demonstrated in Figure 5.3. The patterns obtained for selenized precursor layers

are also included in Figure 5.3a. For the selenized precursors, all the peaks match with orthorhombic Ag<sub>2</sub>Se (PDF 24-1041). The peaks are located at  $2\theta = 22.90^{\circ}$ , 26.80°, 30.89°, 32.80°, 33.53°, 34.79°, 37.10°, 40.05°, 42.62°, 43.37°, 45.38°, 46.80°, 48.40° corresponding to (002), (111), (120), (112), (121), (013), (031), (200), (201), (130), (211), (123) and (014) crystallographic planes respectively of Ag<sub>2</sub>Se. Any of the peaks corresponding to the metal Ag layer was not detected in the samples. This indicates that during dipping in Na<sub>2</sub>SeSO<sub>3</sub> solution, Ag reacted with Se in Na<sub>2</sub>SeSO<sub>3</sub> to form Ag<sub>2</sub>Se [142]. It is known that at acidic pH< 6, dissociation of Na<sub>2</sub>SeSO<sub>3</sub> can precipitate elemental selenium [143] which can be controlled by varying the pH. In our experiment, while dipping in Na<sub>2</sub>SeSO<sub>3</sub> solution of pH~ 4.5, released selenium can react with Ag to form Ag<sub>2</sub>Se at the solution - glass/Sb<sub>2</sub>S<sub>3</sub>/Ag precursor interface [144]. As silver thickness increases from 50 to 100 nm, the Ag<sub>2</sub>Se peaks grow stronger as seen in the figure. After heating, all the Ag<sub>2</sub>Se peaks vanish and new reflections at  $2\theta = 27.15^{\circ}$ ,  $31.44^{\circ}$  and  $45.20^{\circ}$  appear as observed in Figure 5.3b. Comparing with the possible compounds of AgSbS<sub>2</sub> and AgSbSe<sub>2</sub>, these peaks are shifted towards a lower angle from phase pure AgSbS<sub>2</sub> (PDF-17-0456) (dashed vertical lines) and higher angle from pure AgSbSe<sub>2</sub> (PDF-89-3670, dotted vertical lines), both fcc form. Considering the shift, the peaks are assigned to that of cubic AgSbS<sub>2-x</sub>Se<sub>x</sub> [99,142] in correlation with our previous reports. As silver content increases from 50 to 100 nm, the intensity of all the peaks improves and then reduces for Ag thickness 110 nm. Also, some feeble peaks from monoclinic AgSbS<sub>2</sub> are present in AgSb<sub>2-x</sub>Se<sub>x</sub> with 110 nm silver thickness. The zoomed image of (200) peak is depicted in the inset of Figure 5.3b. Analyzing the peak position, the shift is more towards cubic AgSbS<sub>2</sub> showing the sulfur rich solid solution, with stoichiometric formula AgSbS<sub>2</sub>- $_x$ Se<sub>x</sub>. The value of x is 0.58, 0.62, and 0.64 for the films with Ag- 50, 100 and 110 nm respectively. Hence the solid solution stoichiometry can be written as AgSbS<sub>1.42</sub>Se<sub>0.58</sub> (Ag-50 nm), AgSbS<sub>1.38</sub>Se<sub>0.62</sub> (Ag-100 nm) and AgSbS<sub>1.36</sub>Se<sub>0.64</sub> (Ag-110 nm). From Williamson-Hall (W-H) plot, microstrain ( $\epsilon$ ) and crystallite size (D) of the films were calculated. The plots are given in Figure 5.4. The calculated microstrain( $\epsilon$ ) values are  $1.7 \times 10^{-2}$ ,  $6.3 \times 10^{-3}$  and  $1 \times 10^{-2}$  for 50AgSbSSe, 100AgSbSSe, 110AgSbSSe films respectively. The crystallite size values of these samples are 53, 69 and 55 nm. Among the samples, highest crystallite size and smaller microstrain is observed for 100AgSbSSe film, which can be due to higher crystallinity and less lattice imperfections compared to other samples.



Figure 5.3 XRD patterns of (a) selenized glass/Sb<sub>2</sub>S<sub>3</sub>-Ag thin film(b) post-annealed for 350°C for 30 minutes in vacuum with Ag thickness 50, 100 and 100 nm (50AgSbSSe, 100AgSbSSe, 110AgSbSSe). Also, zoomed image of (200) peaks in the inset). The standard patterns of cubic AgSbS<sub>2</sub> and AgSbSe<sub>2</sub> are also included.





Figure 5.4 Williamson- Hall plot of 50AgSbSSe, 100AgSbSSe and 110AgSbSSe thin films.

Further we evaluated the films formed by heating the precursor layers of glass/Sb<sub>2</sub>S<sub>3</sub>. Ag<sub>2</sub>Se with Ag thickness 50 and 100 nm formed by varying selenization time. The seleniztaion time was varied from 1 to 30 minutes. Figure 5.5a shows the XRD patterns of 100AgSbSSe1, 100AgSbSSe5, 100AgSbSSe15 and 100AgSbSSe20 films (samples with Ag thickness 100 nm and selenization time 1, 5, 15 and 20 minutes). The samples showed peaks corresponding to AgSbS<sub>2-x</sub>Se<sub>x</sub> along with small peaks of AgSbS<sub>2</sub> (monoclinic). This can be due to the depletion of selenium available in the bath during the precursor layer formation as selenium precipitates with time.

Figure 5.5b illustrates the XRD patterns of 50AgSbSSe1, 50AgSbSSe5, 50AgSbSSe15, 50AgSbSSe20 and 50AgSbSSe30. The samples selenized at the lower time such as 1 and 5 minutes shows Sb<sub>2</sub>S<sub>3</sub> peaks, which could be due to the insufficient amount of Se to form quaternary. These films were not considered for further studies due to the absence of phase pure compound formation. For all other films, three major peaks at  $2\theta = 27.02^{\circ}$ ,  $31.28^{\circ}$  and  $45^{\circ}$ correspond to (111), (200) and (220) planes of AgSbS<sub>2</sub> and AgSbSe<sub>2</sub> (standard lines marked as vertical lines) forming a solid solution of AgSbS<sub>2-x</sub>Se<sub>x</sub>, as discussed. In general, these three peaks are shifted more towards AgSbSe<sub>2</sub> compared to that of the 10 min selenized samples (50AgSbSSe). In the inset, the normalized (200) peaks indicate that in

50AgSbSSe30 sample the peak shifts more towards AgSbSe<sub>2</sub>. The x values are 0.72, 0.78 and 0.84 for 50AgSbSSe15, 50AgSbSSe20 and 50AgSbSSe30 samples. The equivalent solid solution can be written as AgSbS<sub>1.28</sub>Se<sub>0.72</sub>, AgSbS<sub>1.24</sub>Se<sub>0.78</sub> and AgSbS<sub>1.16</sub>Se<sub>0.84</sub>. The microstrain and crystallite size calculated from W-H plot are given in Figure 5.6. The microstrain values for the films are  $5.3 \times 10^{-3}$ ,  $9.9 \times 10^{-3}$ , and  $1 \times 10^{-2}$ . The average crystallite size for each film is 70, 64 and 46 nm. The microstrain increases with the selenization time and at the same time crystallite size decreases and hence the highest crystallinity for 50AgSbSSe15 films.



Figure 5.5 XRD patterns of heated glass/Sb<sub>2</sub>S<sub>3</sub>-Ag<sub>2</sub>Se films with a) 100 nm Ag layer and dip selenization for 1, 5-, 15- and 20-minutes b) 50 nm Ag thickness dip selenization for 1, 5, 15, 20 and 30 minutes, normalized (200) peak is present in the inset.



Figure 5.6 Williamson- Hall plot of 50AgSbSSe15, 50AgSbSSe20 and 50AgSbSSe30 thin films.

#### 5.1.2 Elemental composition and chemical state

The high-resolution core level spectra of  $AgSbS_{2-x}Se_x$ , as prepared and heated samples were analyzed. For the calculation of relative composition, the background counts were fitted with Shirley type background base line. The XPS spectra of Ag 3d, Sb 3d, S 2p, and Se 3d of selenized precursor glass/Sb<sub>2</sub>S<sub>3</sub> - Ag<sub>2</sub>Se with Ag = 100 nm is shown in Figure 5.7a-d. In this case, the Ag 3d<sub>5/2</sub> and Ag 3d<sub>3/2</sub> peaks are detected at 368.41 eV and 374.41 eV ascribed to Ag<sup>+</sup> state in Ag<sub>2</sub>Se [142]. We can notice that no loss peaks are present in this case. Figure 5.7b illustrates Sb 3d doublets, in which the dominant Sb 3d<sub>5/2</sub> and Sb 3d<sub>3/2</sub> binding energies correlate with  $Sb^{3+}$  state. The peaks at lower energies labelled as I and II are metallic Sb. As given in Figure 5.7c, peaks S  $2p_{3/2}$  and S  $2p_{1/2}$  are in consistent with the S<sup>2-</sup> state in Sb<sub>2</sub>S<sub>3</sub> [123,134]. Peaks observed at 54.33 eV and 55.16 eV in Figure 5.7d is of Se  $3d_{5/2}$  and  $3d_{3/2}$  respectively with separation of 0.83 eV. Also, overlapping with S 2p region, Se 3p doublet is also identified as marked in the figure which also confirms the presence of selenium.

To study the chemical state of Ag, Sb, S, and Se in the quaternary solid solution, the respective core level spectra of 100AgSbSSe and 50AgSbSSe were analyzed as depicted in Figure 5.8 and Figure 5.9 respectively. The XPS survey of AgSbSSe100 sample is given in Figure 5.8a. The survey pattern reveals the presence of C, Ag, Sb, S, and Se on the surface of a typical AgSbS<sub>2-x</sub>Se<sub>x</sub> sample. In the figure, Ag  $3d_{5/2}$  and  $3d_{3/2}$  peaks at binding energies 367.98 eV and 367.98 eV in 50AgSbSSe, 368.15 eV and 374.15 eV in 100AgSbSSe, show a shift towards lower energies compared to elemental Ag 3d indicating the formation of the compound [100], valence charge density is increased compared to that of pure Ag metal. The strong peaks located at 529.08 and 538.42 in Ag = 50 nm and 529.99 eV and 539.33 eV in Ag = 100 nm samples are assigned to Sb  $3d_{5/2}$  and  $3d_{3/2}$  states. Further, the minor peaks I and II at 527.80 eV and 537.30 eV in Ag = 50 nm and 528.44 eV and 537.99 eV in Ag =100 nm samples are assigned metallic Sb<sup>0</sup> state respectively. The peaks of S  $2p_{3/2}$  (161.08 and 160.30 eV) and 2p<sub>1/2</sub> (162.30 and 161.51 eV) depicted in Figure 5.8d and Figure 5.9c respectively, show a peak shift in comparison with the reported values of Sb<sub>2</sub>S<sub>3</sub> implying different chemical environment. Another doublet at 159.75 eV and 165.48 eV in Ag = 50 and 158.88 eV and 164.77 eV in Ag = 100 nm sample corresponds to Se  $3p_{3/2}$  and Se  $3p_{1/2}$ . Also, given in Figures 5.8e and 5.9d the peaks at 54.45 eV, 55.28 eV and 54.33 eV, 55.16 eV are assigned to Se 3d<sub>5/2</sub> and 3d<sub>3/2</sub>. The binding energy shift of Ag 3d, Sb 3d, Se 3d and S 2p peaks confirms the formation of compounds AgSbS<sub>1.42</sub>Se<sub>0.58</sub>, and AgSbS<sub>1.38</sub>Se<sub>0.62</sub> [99,142] in agreement with the XRD results.



Figure 5.7 High resolution XPS spectra of (a) Ag 3d, (b) Sb 3d, (c) S 2p, (d) Se 3d of  $glass/Sb_2S_3-Ag_2Se$  thin film after one cycle of etching.



Figure 5.8 XPS a) survey spectra and core level spectra of (b) Ag 3d, (c) Sb 3d, (d) S 2p, (e) Se 3d of 100AgSbSSe after one cycle of etching.



Figure 5.9 XPS core level spectra of (a) Ag 3d, (b) Sb 3d, (c) S 2p, (d) Se 3d of 50AgSbSSe.

Further, the XPS depth profile analysis and composition of glass/Sb<sub>2</sub>S<sub>3</sub>.Ag<sub>2</sub>Se and 100AgSbSSe films are given in Figure 5.10a-b and Figure 5.10c-d respectively. The depth profile analysis for the glass/Sb<sub>2</sub>S<sub>3</sub>-Ag<sub>2</sub>Se precursor shows that the surface is dominated by Ag and Se signals, with Sb and S signals being noisy, as shown in Figure 5.10a. The same trend can be seen in the depth profile composition in Figure 5.10b, where Ag and Se concentrations are higher near the surface. Analyzing the depth profile of 100AgSbSSe data in Figure 5.10c shows uniform distribution of Ag, Sb, S, and Se elements throughout the depth of the film. Oxygen and Si peak appear at the substrate region. The interlayer diffusion

of  $Ag_2Se$  and  $Sb_2S_3$  layer to form  $AgSbS_{2-x}Se_x$  (in this case  $AgSbS_{1,38}Se_{0.62}$ ) phase is visible from the compositional analysis in Figure 5.10d.



Figure 5.10 XPS depth profile and for composition of the film for Ag 3d, Sb 3d, Se 3d and S 2p in Ag<sub>2</sub>Se-Sb<sub>2</sub>S<sub>3</sub> a) and b), 100AgSbSSe thin films c) and (d) respectively.

Figure 5.11a-h represents XPS spectra of AgSbS<sub>2-x</sub>Se<sub>x</sub> samples with Ag thickness of 40 nm and 80 nm. In 40 nm sample (Figure 5.11a-d) The Ag 3d peaks are observed at 368.51 eV and 374.51 eV and Sb 3d peaks at 528.85 eV and 538.21 eV. The S 2p peaks occur at 161.62 eV and 162.82 eV and Se 3p peaks are assigned at binding energies of 160.11eV and 166.11 eV corresponding to Se  $3p_{3/2}$  and Se  $3p_{1/2}$  respectively confirming the formation of sulfo-selenide [99,142]. The Se 3d peaks are observed at 54.16 eV and 54.99 eV with a binding energy difference of 0.83 eV. In 80 nm (Figure5.11(e-h)) samples, Ag  $3d_{5/2}$  peaks are observed at 368.47 eV and Ag  $3d_{3/2}$  at 374.47 eV and are comparable with the reported values for Ag  $3d_{5/2}$  (368.2 eV) and Ag  $3d_{3/2}$  (374.2 eV) Ag<sup>+</sup> state [145]. The Sb 3d, S 2p and Se 3d peak values are obtained as per the literatures mentioned for 80 nm sample and confirms formation compound.

The XPS core level spectra of Ag 3d, S 2p, Sb 3d and Se 3d of 50AgSbSSe15, 50AgSbSSe20 and 50AgSbSSe30 samples are presented in Figures 5.12, 5.13 and 5.14 respectively. In all the samples Ag shows Ag 3d doublet which constitutes Ag  $3d_{5/2}$  and Ag  $3d_{3/2}$  with binding energy separation of 6 eV.  $Sb_{5/2}$  and  $Sb_{3/2}$  doublets of Sb 3d in the samples are separated by 9.34 eV. The binding energy values of these peaks show a shift in comparison with Sb 3d in as prepared sample due to the different chemical environment. The minor peaks (I and II) are assigned to metallic Sb (Sb<sup>0</sup> state). The deconvoluted peak of S  $2p_{3/2}$  and S  $2p_{1/2}$  peaks have a binding energy separation of 1.21 eV and a binding energy as reported previously [99]. Another doublet peak of Se  $3p_{3/2}$  and Se  $3p_{1/2}$  is also present in the same region. The peaks Se 3d peaks are deconvoluted to Se  $3d_{5/2}$  and Se  $3d_{3/2}$  with binding energy separation 0.83 eV.



Figure 5.11 XPS core level spectra of 40(a-d) and 80 nm (e-h) AgSbS<sub>2-x</sub>Se<sub>x</sub> films. Reproduced with kind permission from Elsevier [109].



Figure 5.12 XPS spectra of the core levels of (a) Ag 3d, (b) Sb 3d, (c) S 2p, (d) Se 3d of 50AgSbSSe15.



Figure 5.13 XPS spectra of the core levels of (a) Ag 3d, (b) Sb 3d, (c) S 2p, (d) Se 3d of 50AgSbSSe20.



Figure 5.14 XPS spectra of the core levels of (a) Ag 3d, (b) Sb 3d, (c) S 2p, (d) Se 3d of 50AgSbSSe30.

The binding energy values of Ag, Sb, S and Se in all the samples is given in the table below. Table 5.1 Binding energy values of Ag, Sb, S and Se.

Element	Compound	Binding energy (eV)		
		3d <sub>5/2</sub>	3d <sub>3/2</sub>	
	$AgSbS_{1.66}Se_{0.34}$	368.51	374.51	
	AgSbS <sub>1.42</sub> Se <sub>0.58</sub>	368.41	374.41	
	AgSbS <sub>1.44</sub> Se <sub>0.56</sub>	368.47	374.47	
Ασ	AgSbS <sub>1.38</sub> Se <sub>0.62</sub>	368.15	374.15	
115	AgSbS <sub>1.28</sub> Se <sub>0.72</sub>	368.23	374.23	
	AgSbS <sub>1.24</sub> Se <sub>0.78</sub>	368.08	374.08	
	AgSbS <sub>1.16</sub> Se <sub>0.84</sub>	368.28	374.28	

	AgSbS <sub>1.66</sub> Se <sub>0.34</sub>	528.58	539.92
Sb	AgSbS <sub>1.42</sub> Se <sub>0.58</sub>	529.08	538.42
	AgSbS <sub>1.44</sub> Se <sub>0.56</sub>	529.20	538.54
	AgSbS <sub>1.38</sub> Se <sub>0.62</sub>	529.99	539.33
	AgSbS <sub>1.28</sub> Se <sub>0.72</sub>	529.59	538.93
	AgSbS <sub>1.24</sub> Se <sub>0.78</sub>	529.13	538.47
	AgSbS <sub>1.16</sub> Se <sub>0.84</sub>	529.71	539.05
		2p <sub>3/2</sub>	2p <sub>1/2</sub>
	$AgSbS_{1.66}Se_{0.34}$	161.62	162.83
	$AgSbS_{1.42}Se_{0.58}$	161.08	162.30
S	AgSbS <sub>1.44</sub> Se <sub>0.56</sub>	160.70	161.91
5	AgSbS <sub>1.38</sub> Se <sub>0.62</sub>	160.30	161.51
	AgSbS <sub>1.28</sub> Se <sub>0.72</sub>	161.60	162.71
	AgSbS <sub>1.24</sub> Se <sub>0.78</sub>	161.35	162.50
	AgSbS <sub>1.16</sub> Se <sub>0.84</sub>	161.42	162.63
		3d <sub>5/2</sub>	3d <sub>3/2</sub>
Se	$AgSbS_{1.66}Se_{0.34}$	54.16	54.99
	AgSbS <sub>1.42</sub> Se <sub>0.58</sub>	53.55	54.40
	AgSbS <sub>1.44</sub> Se <sub>0.56</sub>	54.10	54.93
	AgSbS <sub>1.38</sub> Se <sub>0.62</sub>	54.45	55.28
	AgSbS <sub>1.28</sub> Se <sub>0.72</sub>	53.89	54.72
	AgSbS <sub>1.24</sub> Se <sub>0.78</sub>	53.75	54.56
	AgSbS <sub>1.16</sub> Se <sub>0.84</sub>	53.88	54.71

The atomic percentage of each element present in the sample was determined using EDX analysis. Table 5.2 shows the Ag/Sb and Se/S ratio calculated from the atomic percentage of  $AgSbS_{2-x}Se_x$  samples with different silver thickness and selenization time. The EDX mapping of the samples are given in Figure 5.15.







Figure 5.15 EDX mapping of a)50AgSbSSe b)100AgSbSSe c)110AgSbSSe d)50AgSbSSe15 e) 50AgSbSSe20 and f) 50AgSbSe30.

Sample	Atomic percentage					
	Ag	Sb	S	Se	Ag/Sb	Se/S
Ag- 40	20	30	33.50	16.50	0.66	0.49
Ag-50	21	28	33	18	0.75	0.54
Ag-60	22	27	33	18	0.81	0.54
Ag-80	26	25	30	19	1.04	0.63
Ag-100	25	26	30	19	0.96	0.63
Ag-110	26	25	31	18	1.04	0.58
Se-15 (Ag -50 nm)	21	29	30	20	0.72	0.66
Se-20 (Ag -50 nm)	23	28	29	20	0.82	0.68
Se-30 (Ag -50 nm)	22.5	28.5	28	21	0.78	0.75

Table 5.2 EDX analysis to show the atomic percentage of each element present in thin films.

### 5.1.3 Morphology

SEM images of the selenized precursors and samples and the films formed after heating (50AgSbSSe, 100AgSbSSe and 110AgSbSSe) are depicted in Figure 5.16. The surface morphologies of selenized precursor sample of Ag thickness 50 nm (Figure 5.16a), 100 nm (Figure 5.16c) and 110 nm (Figure 5.16e) are composed of less compact spherical Ag<sub>2</sub>Se grains [99]. As the Ag thicknesses increases, the morphology is more compact and has uniform surface coverage. After heating, surface coverage increases, and the interconnected larger grains are observed for AgSbS<sub>2-x</sub>Se<sub>x</sub> films with varying silver thickness 50 nm (Figure 5.16b), 100 nm (Figure 5.16d), and 110 nm (Figure 5.16f) respectively. For 100 nm sample, the surface is composed of enlarged grains and dispersed crystallites with

square facets. For 110 nm Ag film, less dense surfaces with discontinuous and irregularly shaped structures can be seen.



Figure 5.16 Scanning electron micrographs of  $Ag_2Se-Sb_2S_3$  precursor layers with varying silver thickness and the respective  $AgSbS_{2-x}Se_x$  films formed a)  $Ag_2Se-Sb_2S_3$  with Ag 50 nm b) 50AgSbSSe (AgSbS<sub>1.42</sub>Se<sub>0.58</sub>) c)  $Ag_2Se-Sb_2S_3$  with Ag 100nm d) 100AgSbSSe (AgSbS<sub>1.38</sub>Se<sub>0.62</sub>) e)  $Ag_2Se-Sb_2S_3$  with Ag 110 nm and f) 110AgSbSSe (AgSbS<sub>1.36</sub>Se<sub>0.64</sub>).

Figure 5.17. a-f indicates the SEM images of Ag<sub>2</sub>Se-Sb<sub>2</sub>S<sub>3</sub> precursor with Ag 50 nm layers and AgSbS<sub>2-x</sub>Se<sub>x</sub> films with varying selenization time (50AgSbSSe15, 50AgSbSSe20 and 50AgSbSSe30). Figure 5.17. a, c, d represents Ag<sub>2</sub>Se-Sb<sub>2</sub>S<sub>3</sub> precursor with Ag 50 nm layers formed by varying selenization time. Irregularly shaped, smaller Ag<sub>2</sub>Se grains are

observed in these samples. As the selenization increases, irregularity of the grains also increases. The images of 50AgSbSSe15 ( $AgSbS_{1.28}Se_{0.72}$ ), 50AgSbSSe20 ( $AgSbS_{1.24}Se_{0.78}$ ) and 50AgSbSSe30 ( $AgSbS_{1.16}Se_{0.84}$ ) are given in Figure 5.17b, d, f respectively. A void free surface with uniformly distributed larger grains is seen in these cases.



Figure 5.17 SEM images of AgSbS<sub>2-x</sub>Se<sub>x</sub> films with Ag 50 nm selenized for different time a) Ag<sub>2</sub>Se-Sb<sub>2</sub>S<sub>3</sub> (15 min) b) 50AgSbSSe15 (AgSbS<sub>1.28</sub>Se<sub>0.72</sub>) c) Ag<sub>2</sub>Se-Sb<sub>2</sub>S<sub>3</sub> (20 min) d) 50AgSbSSe20(AgSbS<sub>1.24</sub>Se<sub>0.78</sub>) e) Ag<sub>2</sub>Se-Sb<sub>2</sub>S<sub>3</sub> (20 min) f) 50AgSbSSe30 (AgSbS<sub>1.16</sub>Se<sub>0.84</sub>).

The SEM images of samples with Ag thickness 10, 40, 60 and 80 nm are given in Figure 5.18(a-h). All the films show irregularly shaped spherical grains with improved surface uniformity with Ag thickness. As the Ag thickness increases from 10 to 80 nm, the film compactness and grain size also increase. This can be due to an improvement in the crystallinity of the films. These findings are consistent with previous report [146].



Figure 5.18 SEM images of SEM images of a) 10 nm, b) 40 nm, c) 60 nm and d) 80 nm films. Reproduced with kind permission from Elsevier [109].

The cross-sectional SEM images of glass/Sb<sub>2</sub>S<sub>3</sub>-Ag<sub>2</sub>Se precursor and AgSbS<sub>2-x</sub>Se<sub>x</sub> /glass layers are given in Figure 5.19a-b. The cross-section images clearly show the conversion of layered precursor into homogeneous quaternary compound.



Figure 5.19 SEM cross section of glass/Sb<sub>2</sub>S<sub>3</sub>-Ag<sub>2</sub>Se and AgSbS<sub>2-x</sub>Se<sub>x</sub>/glass layers.
## 5.1.4 Optical properties: Bandgap tuning by varying S/Se ratio

The optical properties of the films were measured, and the bandgap was calculated from transmittance and reflectance spectra (described in section 3.4.7). The reflectance and transmittance spectra of the films are given in Figure 5.20 I. The absorbance and Tauc plots of 50AgSbSSe, 100AgSbSSe and 110AgSbSSe samples are given in Figure 5.21. The thickness corresponding to each film is 337, 387 and 397 nm for 50AgSbSSe, 100AgSbSSe, and 110AgSbSSe respectively. The absorption edge of the film is at ~750 – 900 nm range, with a direct bandgap 1.60, 1.52 and 1.53 eV for 50AgSbSSe, 100AgSbSSe and 110AgSbSSe respectively, suitable for the photovoltaic absorber. The decrease in bandgap values of AgSbS<sub>2-x</sub>Se<sub>x</sub> due to Se incorporation can be attributed to larger size of Se which can reduce orbital overlapping and hence the bandgap [147]. The results are comparable with previous reports, in which bandgap decreases with Se concentration in Sb<sub>2</sub>(S, Se)<sub>3</sub> and CZTSSe thin films [148–150].



Figure 5.20 Reflectance and transmittance spectra of I, a)50AgSbSSe b)100AgSbSSe c)110AgSbSSe and II a) 50AgSbSSe15 b) 50AgSbSSe20 c) 50AgSbSSe30.



Figure 5.21 Absorption spectra of 50AgSbSSe, 100AgSbSSe and 110AgSbSSe films, the respective Tauc plots and bandgap values are given in inset.

The absorption spectra and the optical bandgap of 50AgSbSSe15, 50AgSbSSe20 and 50 AgSbSSe30 samples are presented in Figure 5.22. All the samples show an absorption edge at the 750-950 nm range with measured thickness value 375, 400 and 445 nm for 50AgSbSSe15, 50AgSbSSe20 and 50AgSbSSe30 samples respectively. The bandgap calculation using Tauc plot is given in the inset, 1.55, 1.54 and 1.45 eV. The trend in bandgap value can be explained based on characteristics such as better crystallinity with increase in selenium content can reduce the respective bandgap values due to size confinement effect.



Figure 5.22 Absorption spectra of 50AgSbSSe15, 50AgSbSSe20 and 50AgSbSSe30 films, the respective Tauc plots and bandgap values are given in inset.

The transmittance, reflectance and absorbance spectra of the AgSbS<sub>2-x</sub>Se<sub>x</sub> films with Ag thickness 40, 60 and 80 nm are given in Figure 5.23 and Figure 5.24 respectively. With the increase in Ag thickness the absorption edge shows a shift towards a longer wavelength. The measured film thickness was 330, 350, and 370 nm for samples with Ag thicknesses of 40, 60, and 80 nm, respectively. The Tauc for bandgap calculation is given in the inset of absorption spectra. The values are 1.60, 1.57 and 1.53 eV for the samples. Bandgap values decrease with an increase in silver thickness, this can be due to shift in absorption edge towards longer wavelength with Ag thickness [146].

In our  $AgSbS_{2-x}Se_x$  films, band gap varied from 1.60 to 1.45 eV by increasing x from 0.34 to 0.84 by adjusting the silver layer thickness or the selenization dipping time for a given  $Ag_2Se/Sb_2S_3$  film.



Figure 5.23 T and R spectra of films with Ag - 40, 60 and 80 nm.



Figure 5.24 Optical absorption spectra of  $AgSbS_{2-x}Se_x$  films, Tauc plot is given in the inset. Reproduced with kind permission from Elsevier [109].

# **5.1.5 Electrical studies**

Figure 5.25 a-f depicts the photoresponse of  $AgSbS_{2-x}Se_x$  films. The results were recorded continuously in 20 s intervals under dark, illumination by a 50 W halogen lamp, and after turned off the illumination, at a bias voltage of 0.5 V. Figure 5.25 represents

photocurrent response of 50AgSbSSe, 100AgSbSSe, 110AgSbSSe, 50AgSbSSe15, 50AgSbSSe20 and 50AgSbSSe30 films. The thin films show photocurrent values in the order of 10<sup>-8</sup> A. The calculated photosensitivity values were 143, 196, 52, 202, 164 and 116 % respectively. The photocurrent values increase with Se content, which can be due to the improved crystallinity observed from XRD and SEM in accordance with the previous reports [150,151]. The higher photosensitivity of 50AgSbSSe15 can be due to the combined effect of optimum bandgap and improved crystallinity and thereby better generation and transport of charge carriers. The photocurrent response of 100AgSbSSe15 and 100AgSbSSe20 films are given in Figure 5.26a-b. The photosensitivity values are 48% and 53% for 100AgSbSSe15 and 100AgSbSSe20 films respectively.



Figure 5.25 Photocurrent response curves of  $AgSbS_{2-x}Se_x$  thin films with different Ag thickness  $50AgSbSSe(AgSbS_{1.42}Se_{0.58})$ ,  $100AgSbSSe(AgSbS_{1.38}Se_{0.62})$ , 110AgSbSSe (AgSbS1.36Se\_{0.64}) and varying selenization time  $50AgSbSSe_{1.28}Se_{0.72}$ )  $50AgSbSSe_{20}(AgSbS_{1.24}Se_{0.78})$  and  $50AgSbSSe_{30}(AgSbS_{1.16}Se_{0.84})$ .



Figure 5.26 Photoresponse curves of  $AgSbS_{2-x}Se_x$  with Ag = 100 nm and varying selenization time a) 100AgSbSSe15 (AgSbS\_{1.36}Se\_{0.64} and b) 100AgSbSSe20 (AgSbS\_{1.35}Se\_{0.65}).

We also did the Hall effect measurements of these films. The measured carrier concentration, carrier mobility and conductivity of the films are tabulated below. The positive Hall coefficients represent p-type conductivity of the thin films.

Sample	Carrier concentration (cm <sup>-3</sup> ) ×10 <sup>18</sup>	Hall mobility (cm <sup>2</sup> /V. s)	Dark Conductivity (Ωcm) <sup>-1</sup> ×10 <sup>-3</sup>
50AgSbSSe	9.5	20	1.5
100AgSbSSe	24	40	3.1
110AgSbSSe	8.7	19	1.2
50AgSbSSe15	60	50	4.7
50AgSbSSe20	14	46	1.1
50AgSbSSe30	9.3	33	1.0

Table 5.3 Carrier concentration, Hall mobility and conductivity values of AgSbS<sub>2-x</sub>Se<sub>x</sub> films.

Analyzing the table, we can observe that the mobility changes with the x value. This can be due to the change in the crystallite size and lattice deformation with change in Se/S ratio. The shallow defect concentrations which produce the p-type conductivity may also be varied due to changes in x. The presence of selenium interstitial may be the dominant defect in this material. The increase in conductivity with Se concentration can be directly related to the enhanced mobility-carrier concentration product value from the measurements. Thus, among all the samples 50AgSbSSe15 film with composition AgSbS<sub>1.28</sub>Se<sub>0.72</sub> possesses the highest value of carrier concentration-carrier mobility product.

# **5.1.6 Photodetectors**

Photodetectors were fabricated using  $AgSbS_{2-x}Se_x$  thin films with Ag thickness 40, 60 and 80 nm. The photocurrent response of  $AgSbS_{2-x}Se_x$  photodetectors was measured using LEDs of different wavelengths and laser of different power densities. The schematic representation of photodetector (photoconductive mode) is given in Figure 5.27.



Figure 5.27 Schematic of AgSbS<sub>2-x</sub>Se<sub>x</sub> photodetector.

Figure 5.8 shows the photocurrent response of the samples as measured with LEDs of various wavelengths at a bias voltage of 1 V. The experiments were performed with 465, 520, 590, and 620 nm LEDs for 10 seconds in the dark, 10 seconds under illumination, and then another 10 seconds in the dark. For each sample using an LED of a different wavelength, a significant difference in photocurrent values was seen. The sample with 80 nm of Ag thickness resulted highest photo response value, which may be caused by the lowest bandgap and hence highest absorption above the band edge. For all of the samples, the cyclic response shown in the figure shows a constant rate of photocurrent decay, which supports the material's stability [152] and reproducibility of the material for photodetector applications .



Figure 5.28 (a) Photoresponse of the samples using 465 nm, 520 nm, 590 nm and 620 nm LEDs (b) cyclic photoresponse of the same samples. Reproduced with kind permission from Elsevier [109].

Table 5.4 shows the calculated photosensivity values for the samples. A graph, sensitivity vs wavelength, is plotted from the tabulated photosensitivity values (Figure 5.29). According to the graph, 40 and 60 nm samples have nearly the same range of sensitivity, which is higher than the 80 nm sample. The presence of trap states, as well as the metallic nature caused by the high Ag content, could be the explanations. Based on these findings, the 60 nm sample is the best for photodetection applications due to its higher sensitivity and photocurrent values when compared to other samples. The samples' rise and decay times were calculated using the photoresponse [153]. For 80, 60, 40, and samples, the rise times were 0.45, 1.86, and 1.33, and the decay times were 5.27, 4.40, and 4.23, respectively.



Figure 5.29 Sensitivity vs wavelength plot for different samples. Reproduced with kind permission from Elsevier [109].

The photoresponse of the samples was also measured using 532 nm continuous laser for different powers. The laser powers were varied from 8 mW to 24 mW by multiples of 4 and from 10 to 60 mW by multiples of 10. The photoresponse of the samples with bias voltage 0.5 V and laser power varying from 8 to 24 mW is presented in Figure 5.30. The photoresponse of the same samples with power densities varying from 6.06 to 45.45 mW/cm<sup>2</sup> is shown in Figure 5.31.



Figure 5.30 Photoresponse to various laser powers ranging from 8 mW-24 mW and bias voltage of 0.5 V. Reproduced with kind permission from Elsevier [109].



Figure 5.31 Photoresponse to lasers with power densities ranging from  $6.06 - 45.45 \text{ mW/cm}^2$  (applied voltage 0.5 V). Reproduced with kind permission from Elsevier [109].

The responsivity of the sample was measured using the equation given below.

$$R = \frac{I_{\lambda}}{P \times S} \tag{16}$$

where  $I_{\lambda} = I_{\text{light}} - I_{\text{dark}}$ , P is the optical power density, calculated by dividing the laser power by the area of the beam and S is the electrode area. The change in responsivity with power densities corresponding to laser powers from 8 to 60 mW is depicted in Figure 5.32a. Figure 5.32b indicates the sensitivity dependence of power density from 10 to 60 mW power.



Figure 5.32 Plot of a) responsivity vs power density b) sensitivity vs power density, with varying power. Reproduced with kind permission from Elsevier [109].

 $I_{\lambda}$  and sensitivity values obtained for the LEDs of different wavelengths and responsivity and sensitivity obtained for the different laser power densities is given in the Table 5.4.

Sample	LED	$I_{\lambda}(A)$	Sensitivity	Laser	Responsivity	Sensitivity
	used	×10 <sup>-8</sup>	(%)	(532 nm)	$(AW^{-1}) \times 10^{-9}$	(%)
				power (mW)		
Ag	g Applied bias voltage = 1 V		Applied bias voltage = 0.5 V			
thickness						
	Blue	36.5	57.60	8	3.76	24.55
80 nm	Green	27.6	39.42	12	3.95	37.22
	Yellow	17.6	29.79	16	3.97	43.55
	Red	24.4	25.00	20	3.76	51.33
				24	3.62	56.97
				10	4:45	29.00
				20	3.91	53.26
				30	3.31	69.11
				40	2.88	77.85
				50	2.59	86.34
				60	2.33	92.46
	Blue	5.57	163.82	8	6.35	52.11
60 nm	Green	3.89	105.54	12	5.28	67.16
	Yellow	2.57	77.89	16	4.86	82.93
	Red	3.27	60.04	20	4.77	101.88
				24	4.47	112.61
				10	4.97	52.31
				20	4.63	96.01
				30	4.42	130.65
				40	3.76	148.34
				50	3.28	162.29
				60	2.96	176.95

Table 5.4  $I_{\lambda}$ , sensitivity and responsivity obtained for AgSbS<sub>2-x</sub>Se<sub>x</sub> samples with different LEDs and laser powers. Reproduced with kind permission from Elsevier [109].

	Blue	2.93	158.24	8	5.09	58.11
40 nm	Green	2.01	97.26	12	5.29	90.24
	Yellow	1.49	79.43	16	4.75	109.60
	Red	1.83	67.03	20	4.56	136.52
				24	4.26	158.51
				10	5.19	80.09
				20	4.69	143.16
				30	4.10	178.79
				40	3.54	204.43
				50	3.18	226.26
				60	2.88	241.96
			1			

We also measured the photoresponse of the samples using UV LEDs (395 nm) and IR LEDs (740 nm) to show the wide spectral range. The photocurrent response is given in the figure below.



Figure 5.33 The on-off behavior of  $AgSbS_{2-x}Se_x$  photodetector to UV and IR LEDs. Reproduced with kind permission from Elsevier [109].

#### **5.1.7** Photovoltaic device

The solar cells were made using AgSbS<sub>2-x</sub>Se<sub>x</sub> as an absorber layer and CdS as the window layer. The photograph of fabricated solar cell is presented in Figure 5.34a. The active device area was 0.1 cm<sup>2</sup>. The SEM cross section view of 50AgSbSSe15 solar cell before electrode deposition is shown Figure 5.34b. The individual layer of photovoltaic structure can be seen in the figure. The AgSbS<sub>2-x</sub>Se<sub>x</sub> absorber layer with enlarged grains can be observed in the Figure 5.34b. Figure 5.34c shows the J-V curves corresponding to glass/FTO/n-CdS/p-AgSbS<sub>2-x</sub>Se<sub>x</sub> /carbon/silver structure. To prevent the diffusion of Ag from the silver paint into the absorber material, a carbon layer was coated prior to silver electrode. The calculated efficiency for 50AgSbSSe, 100AgSbSSe and 110AgSbSSe are 2.1 %, 3.3% and 1.7%. The photovoltaic parameters are given in Table 5.5, better performance than that reported previously [100]. The J-V characteristics of the solar cells with AgSbS<sub>1.28</sub>Se<sub>0.72</sub>, AgSbS<sub>1.24</sub>Se<sub>0.78</sub> and AgSbS<sub>1.16</sub>Se<sub>0.84</sub> absorber layers of varying selenization time are also presented in Figure 5.34c and the photovoltaic parameters in Table 5.5. The calculated efficiencies are 4.2, 3.3 and 1.8 % for 50AgSbSSe15, 50AgSbSSe20 and 50AgSbSSe30 respectively. AgSbS<sub>2-x</sub>Se<sub>x</sub> films with 100 nm Ag thickness selenized for 15 and 20 min were also incorporated in solar cells (Figure 5.34d), yielding low device performance with efficiency values 1.3 and 2 % respectively for 15 and 20 min selenized samples.



Figure 5.34 a) Schematic representation of glass/FTO/n-CdS/p-AgSbS<sub>2-x</sub>Se<sub>x</sub>/C/Ag solar cell, b) cross section SEM image of a complete solar cell prior to electrode coating, J-V characteristics of solar cells c) using  $AgSbS_{2-x}Se_x$  with different compositions d) 100AgSbSSe15 and 100AgSbSSe20.

Solar cell	V <sub>oc</sub> (mV)	Jsc (mA/cm <sup>2</sup> )	FF	Efficiency (η) %
CdS/50AgSbSSe	570	6.9	0.53	2.1
CdS/100AgSbSSe	510	11	0.58	3.3
CdS/110AgSbSSe	400	7.9	0.54	1.7
CdS/50AgSbSSe15	525	15	0.53	4.2
CdS/50AgSbSSe20	445	15	0.5	3.3
CdS/50AgSbSSe30	465	8	0.47	1.8
CdS/100AgSbSSe15	386	7.9	0.42	1.3
CdS100AgSbSSe20	347	13.6	0.43	2

Table 5.5 Photovoltaic parameters of AgSbS<sub>2-x</sub>Se<sub>x</sub> solar cells.

We also fabricated solar cells with an absorber layer formed by heating glass/Sb<sub>2</sub>S<sub>3</sub>-Ag (50)-Ag (50) and glass/Sb<sub>2</sub>S<sub>3</sub>-Ag (50)-Ag (100) selenized for 10 minutes. The J-V characteristics is given in Figure 5.35a. Further, Figure 5.35b corresponds to the solar cells fabricated from the absorber layer formed by heating glass/Sb<sub>2</sub>S<sub>3</sub>-Ag (50 and 80 nm) selenized by dipping 10 minutes in sodium selenosulfate solution for 2 times. The photovoltaic parameters are given in Table 5.6.



Figure 5.35 J-V characteristics of solar cells with a) 50-50AgSbSSe,50-100AgSbSSe and b) 80AgSbSSe10-10 and 50AgSbSSe10-10 absorber layers.

Solar cell	V <sub>oc</sub> (mV)	J <sub>sc</sub> (mA/cm <sup>2</sup> )	FF	Efficiency (η) %
CdS/50-50AgSbSSe	545	12	0.50	3.2
CdS/50-100AgSbSSe	445	16	0.46	3.3
CdS/50AgSbSSe10-10	484	8.9	0.52	2.2
CdS/80AgSbSSe10-10	425	9.5	0.46	1.8

Table 5.6 Photovoltaic parameters of AgSbS<sub>2-x</sub>Se<sub>x</sub> solar cells.

Figure 5.36 corresponds to the external quantum efficiency measurements for the cell with absorber layer 100AgSbSSe in the wavelength range 300-900 nm. The EQE values below 500 nm shows almost 15%, which is an indication of optical absorption due to CdS window layer. Beyond 500 nm, the EQE value is less than 5 %, which is due to the absorption of 100AgSbSSe layer. The decrease in EQE in larger wavelength region may be due to insufficient and poor collection of carriers, revealing the route for further work to improve  $J_{sc}$  and hence efficiency. Further improvement can be done by enhancing the absorber layer properties, employing efficient contacts and intrinsic layers which can reduce the recombination.



Figure 5.36 External quantum efficiency spectrum (EQE) of device with  $AgSbS_{2-x}Se_x$  absorber layer with silver thickness 100 nm.

Among all the devices fabricated, the one with the best PV performance was used for self-powered photodiode. The cyclic photoresponse measurements of self-powered photodetector with a halogen lamp (50 W power), LEDs of different wavelengths (465, 520 and 590 nm) and 1064 nm (939 mW) laser are given in Figure 5.37. Calculated photosensitivity values are given in the Table 5.7. The cyclic photocurrent measurements show the photosensitivity, stability and reproducibility of the AgSbS<sub>2-x</sub>Se<sub>x</sub> based self-powered photodiode.



Figure 5.37 Cyclic photoresponse of AgSbS<sub>1.28</sub>Se<sub>0.72</sub> photodiode under zero bias with a) halogen lamp, b) LEDs and c) 1064 nm laser.

Source	Sensitivity (%)	
Halogen lamp (50 W)	1622	
465 nm (LED)	800	
520 nm (LED)	650	
590 nm (LED)	522	
1064 nm (LASER)	233	

Table 5.7 Photosensitivity values of AgSbS<sub>1.28</sub>Se<sub>0.72</sub> photodiode under different light sources.

# Selenization mechanism

 $AgSbS_{2-x}Se_x$  films are formed by low vacuum heating of glass/Sb<sub>2</sub>S<sub>3</sub>-Ag<sub>2</sub>Se layers, which are obtained by dip selenization of glass/Sb<sub>2</sub>S<sub>3</sub>-Ag layers. Se/S composition in the compound highly depends on Ag<sub>2</sub>Se formation. The chemical reaction involving the formation of Ag<sub>2</sub>Se can be described by following steps.

First the acetic acid (25%) and water dissociates into hydronium ions ( $H_3O^+$ ) and acetate anions ( $CH_3COO^-$ ).

 $CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$ (17)

In the next step  $Na_2SeSO_3$  (aqueous) was added to the solution. The acetic acid in the solution act as a catalyst and accelerates the hydrolysis of  $Na_2SeSO_3$  to release  $Se^{2-}$  ions [154,155].

$$CH_{3}COO^{-} + H_{3}O^{+} + Na_{2}SeSO_{3} + H_{2}O \rightarrow Na_{2}SeSO_{3} + 2OH^{-} + CH_{3}COOH + 2H^{+} (18)$$

$$Na_2SeSO_3 + OH^- \rightarrow Na_2SO_4 + HSe^-$$
<sup>(19)</sup>

$$HSe^{-} + OH^{-} \rightarrow H_2O + Se^{2-}$$
(20)

Finally, the  $Se^{2-}$  reacts with  $Ag^+$  to form  $Ag_2Se$ .

$$Se^{2} + 2Ag^{+} \rightarrow Ag_{2}Se$$
 (21)

Subsequently, by heating  $Sb_2S_3$ -Ag<sub>2</sub>Se layered structures, AgSbS<sub>2-x</sub>Se<sub>x</sub> films are formed. By this mechanism, for a given thickness of  $Sb_2S_3$ , x can be tuned to values 0.58, 0.62, 0.64 0.72, 0.78 and 0.84 by varying Ag layer thickness and dip selenization time. Depending on the x

value, optical and electrical properties of the films can be changed. The champion device of CdS/ AgSbS<sub>2-x</sub>Se<sub>x</sub> with x = 0.72 yielded an efficiency of 4.2% due the highest grain size, the lowest microstrain and with the most compact morphology of the absorber films. Large grain size and uniform surface morphology can reduce the grain boundary defects and thereby improving the mobility of the charge carriers [156].

In conclusion, we synthesized AgSbS<sub>2-x</sub>Se<sub>x</sub> thin films by heating glass/Sb<sub>2</sub>S<sub>3</sub>-Ag<sub>2</sub>Se layer made from the selenization of glass/Sb<sub>2</sub>S<sub>3</sub>-Ag by solution-based technique. We present cubic phase of the material and has provided evidence through XRD. By adjusting Ag thickness and dip selenization time, the Se/S ratio was systematically controlled. The x values obtained from XRD were 0.34, 0.58, 0.60, 0.56, 0.62, and 0.64 for Ag thicknesses of 40, 50, 60, 80, 100, and 110 nm and 0.72, 0.78, and 0.84 for samples that had been selenized for 15, 20, and 30 minutes. Increasing x from 0.34 to 0.84 caused the optical bandgap to decrease from 1.6 to 1.45 eV, making it appropriate for photovoltaic and photodetector applications. Finally, these films were incorporated in photovoltaic device as an absorber layer. The best device fabricated with AgSbS<sub>1.28</sub>Se<sub>0.72</sub> (x = 0.72) absorber layer had the following photovoltaic parameters:  $V_{oc} = 525$  mV, a  $J_{sc} = 15$  mA/cm<sup>2</sup>, FF = 0.53, and  $\eta = 4.2$  %. AgSbS<sub>2-x</sub>Se<sub>x</sub> thin films with Ag thickness 40, 60 and 80 nm were investigated for photodetection application in UV-Vis-NIR region. A large spectral range of detection is possible with the AgSbS<sub>2-x</sub>Se<sub>x</sub> material.

To increase the Se concentration and to improve the PV performance, we prepared  $AgSbS_{2-x}Se_x$  thin films using Se nanocolloid synthesized by laser irradiation technique. The complete study of  $AgSbS_{2-x}Se_x$  thin films and its applications in PV devices and photodetectors will be discussed in the next chapter.

# CHAPTER 6

# AgSbS<sub>2-x</sub>Se<sub>x</sub> AND GRAPHENE INCORPORATED AgSbS<sub>2-x</sub>Se<sub>x</sub> FILMS USING Se:GRAPHENE NANOCOLLOIDS FOR OPTOELECTRONICS

This chapter explains the preparation AgSb<sub>2-x</sub>Se<sub>x</sub> and graphene incorporated AgSbS<sub>2-x</sub>Se<sub>x</sub> thin films using Se and Se:graphene nanocolloid by laser irradiation in liquid technique, attempts for the better control of x. Se nanocolloids and Se:Graphene (Se:Gr) nanocolloids were spin coated on glass/Sb<sub>2</sub>S<sub>3</sub>-Ag precursor layers. The effect of heating temperature and amount of graphene on the structure, morphology, composition, and optoelectronic properties of the thin films are discussed. These thin films are used to develop photovoltaic and photodetector devices.

# 6.1 Results and discussions

# 6.1.1 Characterization of Se and Se:Gr nanocolloids

The bulk selenium powder dissolved in distilled water (DW), acetone and isopropyl alcohol (IPA) and the Se nanocolloid formed after laser irradiation is presented in Figure 6.1.



Nd;YAG laser  $\lambda = 532 \text{ nm}$ 

Frequency =10 Hz Pulse width = 10 ns Energy = 310 mJ Laser fluence = 0.79 J/cm<sup>2</sup>



Se powder dissolved in different solvents

Se nanocolloid

Figure 6.1 Se powder dissolved in DW, acetone and IPA and Se nanocolloid formed after laser irradiation.

The photographs of Se: Graphene nanocolloid synthesis is given below.



Figure 6.2 Schematic of Se:Graphene nanocolloid.

The synthesized Se nanocolloids were characterized by different techniques. The XRD patterns of bulk selenium powder is given in the Figure 6.3. The peaks well match with hexagonal selenium (pdf-73-0465). No other peaks were detected in XRD, which indicates the purity of Se powder.



Figure 6.3 XRD pattern of bulk selenium powder.

The morphology of the bulk Se powder, Se and Se:Gr nanoparticles were studied using SEM and TEM techniques. SEM images of bulk Se powder, Se nanoparticles and Se:Gr nanoparticles are given in Figure 6.4a-e. Large agglomerated big particles of ~ 1 $\mu$ m in size composed of faceted crystallites are observed in Se powder, whereas smaller spherical particles are observed for Se nanoparticles. The average size of the Se nanoparticles formed in different solvents after laser irradiation is found to be 148-152 nm. When the material in the solution is irradiated by nanosecond pulsed laser, photothermal mechanism of laser fragmentation occurs [157–160]. By absorbing photon energy electrons in the material gets excited. Photon energy will be transferred to lattice. A thermal equilibrium will be attained when this transferred energy becomes equal to lattice energy. At thermal equilibrium, the solution undergoes heating, melting, and evaporation to form nanoparticles. This photothermal mechanism of laser fragmentation is affected by different parameters such as size of nanomaterials and laser fluence. The reduction in size and change in morphology after laser irradiation cause the color change from grey (Se powder dissolved in solvent) to red for nanocolloid.



Figure 6.4 SEM images of a) bulk Se powder, Se nanoparticles after irradiation in different solvents such as b) distilled water c) acetone c) IPA, e) Se:Graphene nanoparticles in IPA.

The SEM images of Se:Graphene nanoparticles show that spherical Se nanoparticles are distributed over graphene layers (Figure 6.4e). Layered structure of graphene is clear from the SEM image.

Further, the morphology of the nanoparticle was studied using TEM. As seen from Figure 6.5 spherical nanoparticles are obtained in all solvents. In acetone and IPA nanoparticles have larger sizes compared to that obtained in distilled water. The TEM images of Se nanoparticles in different solvents are presented in Figure 6.5. The TEM also confirms the formation of spherical Se nanoparticles after laser irradiation.







Figure 6.5 TEM images of Se nanoparticles by laser irradiation in a) DW b) acetone c) IPA and d) EDX.

The elemental analysis of Se nanoparticles was done using EDX analysis. Figure 6.5d indicates Se peaks, no other additional peaks were detected in EDX which confirms purity of the nanocolloid obtained.

#### 6.1.2 Crystal structure and solid solution stoichiometry

The XRD patterns of the sample before heating (Se nanocolloid spin coated over glass/Sb<sub>2</sub>S<sub>3</sub>-Ag precursor layer) is presented in Figure 6.6. For the as prepared sample all the peaks match with hexagonal Se, any of the peaks corresponding to metal Ag was not detected, this can be due to the high concentration of Se nanocolloids over the surface. Since as prepared Sb<sub>2</sub>S<sub>3</sub> is amorphous those peaks were not detected. The XRD patterns of AgSbS<sub>2-x</sub>Se<sub>x</sub> films prepared using 20 ml (single deposition) of Se nanocolloids in different solvents is given in Figure 6.7a. Three major peaks are observed at  $2\theta = 27^{\circ}$ ,  $31.33^{\circ}$  and  $44.90^{\circ}$ . The formation of AgSbS<sub>2-x</sub>Se<sub>x</sub> solid solution was confirmed by comparing the peak position with cubic AgSbS<sub>2</sub> (PDF-17-0456) and AgSbSe<sub>2</sub> (PDF-89-3670) in correlation with previous results [99,142]. The zoomed image of (200) peak (normalized intensity) indicates higher peak intensity for the films formed using nanocolloids in acetone and IPA than in DW. The x value of each film was calculated using Vegard's law. The values are 1.06, 1.10, 1.12 and the corresponding composition AgSbS<sub>0.94</sub>Se<sub>1.06</sub>, AgSbS<sub>0.90</sub>Se<sub>1.10</sub> and AgSbS<sub>0.88</sub>Se<sub>1.12</sub> for films formed using Se nanocolloids in DW, acetone and IPA. AgSbS<sub>2-x</sub>Se<sub>x</sub> thin films formed by this method are rich in selenium than the films formed by dip selenization.

The crystallite size was calculated using the Scherrer formula, and the values are 21, 26 and 27 nm for films formed using Se nanocolloids in DW, acetone and IPA. Se nanocolloids in acetone and IPA were multi-deposited (40 ml) on Ag-Sb<sub>2</sub>S<sub>3</sub>/glass precursor layer to achieve better film thickness and more Se rich AgSbS<sub>2-x</sub>Se<sub>x</sub> solid solution. The XRD patterns of heated films are given in Figure 6.7b. Three major peaks are observed at  $2\theta = 26.89^{\circ}$ , 31.03° and 44.40°. The peak positions indicate the formation of AgSbS<sub>2-x</sub>Se<sub>x</sub> solid solution. From the peak position, shift is more towards AgSbSe<sub>2</sub>, corresponds to Se rich solid solution. This can be clear from the zoomed image of (200) pane in Figure 6.7c. The corresponding stoichiometric formula can be written as AgSbS<sub>0.62</sub>Se<sub>1.38</sub> (acetone) and AgSbS<sub>0.60</sub>Se<sub>1.40</sub> (IPA). The calculated crystallite size values are 29 and 31 nm.



Figure 6.6 XRD patterns of as prepared Se-Ag-Sb<sub>2</sub>S<sub>3</sub>/glass precursor



Figure 6.7 XRD patterns of  $AgSbS_{2-x}Se_x$  thin films using Se nanocolloids in different solvents a) single deposition (20 ml nanocolloid), b) multi deposition (40 ml) c) normalized peak intensity image of (200) peak.

#### **6.1.3 Optical properties**

The optical absorption, transmittance, and reflectance spectra of AgSbS<sub>2-x</sub>Se<sub>x</sub> thin films were measured using UV-Vis-NIR spectroscopy. Figure 6.8a-b indicates the absorbance, reflectance, and transmittance spectra of AgSbS<sub>2-x</sub>Se<sub>x</sub> films formed by a single deposition of Se nanocolloid (20 ml) and Figure 6.8c-d corresponds to absorbance, reflectance and transmittance spectra of AgSbS<sub>2-x</sub>Se<sub>x</sub> with multi-deposited Se nanocolloid. From Figure 6.8a, the absorption edge can be observed around 710-920 nm range. A slight increase in absorbance is observed for films prepared with Se nanocolloid in acetone and IPA than in DW. The measured thickness of the films is 270, 290 and 300 nm for AgSbS<sub>2-x</sub>Se<sub>x</sub> films prepared using Se nanocolloid in different solvents. From the transmittance and reflectance values (Figure 6.8b) the bandgap of the films was calculated by means of Tauc plot and it is given in Figure 6.8e.

The absorption spectra of  $AgSbS_{2-x}Se_x$  films with multi-deposited Se nanocolloid is shown in Figure 6.8c. The onset of absorption is observed around 690-910 nm range. A small increment in the absorption is observed for films formed with Se nanocolloid in IPA. The measured thickness values of the films are 300 and 320 nm for Se nanocolloid in acetone and IPA respectively. The bandgap calculated from transmittance and reflectance is given in Figure 6.8f. The calculated bandgap values are 1.20 and 1.18 eV for the films prepared with Se nanocolloid in acetone and IPA. The decrease in bandgap value in IPA can be due to a slight increase in Se content and crystallinity as observed from XRD.





Figure 6.8 a) absorption b) transmittance and reflectance e) Tauc plot of AgSbS<sub>2-x</sub>Se<sub>x</sub> films prepared by single deposition (20 ml) of Se nanocolloid in DW, acetone and IPA, c) absorption d) transmittance and reflectance f) Tauc plot of AgSbS<sub>2-x</sub>Se<sub>x</sub> films by multi-deposition (40 ml) of Se nanocolloid in acetone and IPA.

#### 6.1.4 Morphology

The morphologies of AgSbS<sub>0.94</sub>Se<sub>1.06</sub>, AgSbS<sub>0.90</sub>Se<sub>1.10</sub>, AgSbS<sub>0.88</sub>Se<sub>1.12</sub>, AgSbS<sub>0.62</sub>Se<sub>1.38</sub> and AgSbS<sub>0.60</sub>Se<sub>1.40</sub> films are presented in Figure 6.9a-e. The films formed using Se nanocolloid in DW represent irregularly shaped grains. Some voids can also be seen on the surface (Figure 6.9a). The thin films prepared using nanocolloids in acetone (Figure 6.9b) and IPA (Figure 6.9c) exhibit compact morphology with smaller spherical grains. Voids free surface with uniformly distributed grains can be seen in Figure 6.9b-c. The films formed by the multi-deposition of Se nanocolloid (acetone and IPA) display bigger spherical particles. The surface coverage has improved after the multi deposition. The films formed from nanocolloid in IPA represent a compact morphology with well-defined boundaries as illustrated in Figure 6.9d.



Figure 6. 9 SEM images of AgSbS<sub>2-x</sub>Se<sub>x</sub> films with different stoichiometry a) AgSbS<sub>0.94</sub>Se<sub>1.06</sub>, b) AgSbS<sub>0.90</sub>Se<sub>1.10</sub>, c) AgSbS<sub>0.88</sub>Se<sub>1.12</sub>, d) AgSbS<sub>0.62</sub>Se<sub>1.38</sub> and e) AgSbS<sub>0.60</sub>Se<sub>1.40</sub>.

# **6.1.5 Electrical properties**

Photoresponse measurements of the films were recorded using a halogen lamp (50 W) by applying a bias voltage of 0.5 V. The photoresponse curve of the films are given in Figure 6.10. The  $AgSbS_{2-x}Se_x$  films of  $(AgSbS_{0.94}Se_{1.06}, AgSbS_{0.90}Se_{1.10}, and$ 

AgSbS<sub>0.88</sub>Se<sub>1.12</sub>) formed by the single deposition of Se nanocolloid in different solvents showed photocurrent in the order of  $10^{-7}$  A. The calculated conductivity and sensitivity values are  $3 \times 10^{-3}$  ( $\Omega$ cm)<sup>-1</sup>,  $3.9 \times 10^{-3}$  ( $\Omega$ cm)<sup>-1</sup>,  $4.3 \times 10^{-3}$  ( $\Omega$ cm)<sup>-1</sup> and 92%, 82%, 83% for AgSbS<sub>0.94</sub>Se<sub>1.06</sub>, AgSbS<sub>0.90</sub>Se<sub>1.10</sub> and AgSbS<sub>0.88</sub>Se<sub>1.12</sub> films, respectively. Among the three films highest value of conductivity and photocurrent values were observed for AgSbS<sub>2-x</sub>Se<sub>x</sub> thin films prepared using Se nanocolloid in IPA.

The photoresponse of the films with multi-deposited  $(AgSbS_{0.62}Se_{1.38}$  and  $AgSbS_{0.60}Se_{1.40}$ ) Se nanocolloid is given in Figure 6.10. The films show photocurrent in the order of  $10^{-7}$  A. The conductivity values are in the order of  $10^{-2}$  ( $\Omega$ cm)<sup>-1</sup>. Improvement in conductivity values are observed for multideposited films compared to single deposited. From the SEM images, larger grains are observed for multideposited films incomaprison with single deposited films. The increases in grain size with Se concentration lowers the density of grain boundaries which in turn improves the flow of charge carriers hence the conductivity [150]. The calculated sensitivity values are 73% and 80% for the films with multideposited Se nanocolloids in acetone and IPA.



Figure 6.10 Photocurrent response of  $AgSbS_{2-x}Se_x$  films with single (20 ml) and multideposition (40 ml) of Se nanocolloid in different solvents

Among all the samples,  $AgSbS_{0.60}Se_{1.40}$  films with multideposited Se nanocolloid in IPA showed the best opto-electronic properties. Further, we studied the effect of heating temperatures on structural, morphology and opto-electric properties of these films.

# 6.1.6 Crystal structure: effect of heating temperature on AgSbS2-xSex thin films

The XRD patterns of films heated at different temperatures are given Figure 6.11. All the samples were measured in grazing incidence mode (GIXRD). The heated samples show 3 major peaks at  $2\theta = 26.86^{\circ}$ ,  $31.13^{\circ}$  and  $44.55^{\circ}$ . Films formed at  $325 \,^{\circ}$ C show additional three feeble peaks at  $33.60^{\circ}$ ,  $34.80^{\circ}$  and  $36.16^{\circ}$  corresponding to Ag<sub>2</sub>Se, no such peaks were observed for 350 and 375 heated samples. A slight reduction in the XRD peak intensity is observed when the heating temperature increased from  $350 \,^{\circ}$ C to  $375 \,^{\circ}$ C. The calculated crystallite size values are 23, 29 and 27 nm. The x value of AgSbS<sub>2-x</sub>Se<sub>x</sub> films are 1.16, 1.34 and 1.30. The corresponding composition of each film can be written as AgSbS<sub>0.84</sub>Se<sub>1.16</sub>, AgSbS<sub>0.66</sub>Se<sub>1.34</sub> and AgSbS<sub>0.70</sub>Se<sub>1.30</sub> for samples heated at  $325 \,^{\circ}$ C,  $350 \,^{\circ}$ C and  $375 \,^{\circ}$ C. The x value indicates the composition of Se in the films.



Figure 6.11 XRD patterns of Se-Ag-Sb<sub>2</sub>S<sub>3</sub>/glass a) as prepared b) heated at 325 °C, 350 °C and 375 °C. The normalized (intensity) (200) peak is given in the inset.

#### 6.1.7 Chemical composition

XPS analysis of AgSbS<sub>2-x</sub>Se<sub>x</sub> films is given in Figures 6.12. The survey spectrum of sample formed by heating at 350 °C (Figure 6.12a) reveals Ag, Sb, S, Se, C and O on the surface. The XPS spectra of Ag, Sb, S and Se is given in Figure 6.12b-d. The core level spectra of Ag  $3d_{5/2}$  and  $3d_{3/2}$  with binding energies 369.69 eV and 375.69 eV, show a shift towards lower energies compared to elemental Ag 3d indicating the formation of the compound [100]. The peaks at 531.27 eV and 540.67 eV were assigned to Sb  $3d_{5/2}$  and  $3d_{3/2}$  states. Further, the minor peaks correspond to Sb<sup>0</sup> state. The S  $2p_{3/2}$  (162.87 eV) and S  $2p_{1/2}$  (164.08 eV) with a peak separation energy of 1.22 eV is depicted in Figure 6.12d is having a peak shift compared with the reported values of Sb<sub>2</sub>S<sub>3</sub>, which is the indication of compound formation. As given in Figure 6.12e the peaks at 53.63 and 54.46 eV are assigned to Se  $3d_{5/2}$  and  $3d_{3/2}$  with a binding energy separation of 0.85 eV. The chemical shift in the binding energy of Ag-3d, Sb-3d, Se-3d and S 2p peaks confirms the formation of the compound AgSbS<sub>0.66</sub>Se<sub>1.34</sub> [99,142]. From the atomic percentage obtained from XPS analysis we calculated the Se/S ratio, and it is found to be 1.20, it shows the Se rich solid solution in accordance with our XRD results.





Figure 6.12 XPS a) survey spectra, high resolution spectra of b) Ag 3d c) Sb 3d d) S 2p e) Se 3d in AgSbS<sub>0.66</sub>Se<sub>1.34</sub>.

Depth profile analysis of the as prepared and sample heated at 350 °C is shown in Figure 6.13a-b. The depth profile of Se-Ag-Sb<sub>2</sub>S<sub>3</sub>/glass (as prepared) precursor layers indicate that (Figure 6.13a) the Ag, Sb, S and Se elements are non-uniformly distributed over the depth. The surface is mainly composed of Ag, Sb and Se peaks. From the third level onwards S 2p peaks can be seen. The Si 2p peak present from 7th level onwards indicate the signals from the substrate. Near the substrate level Se 3d becomes noisy and oxygen peaks can also be seen. Figure 6.13b shows the distribution of elements in  $AgSbS_{0.66}Se_{1.34}$ . All the elements are uniformly distributed throughout the depth. In addition, presence of Si from the substrate only starts from 13<sup>th</sup> etch level.



Figure 6.13 XPS depth profile for Ag 3d, Sb 3d, Se 3d and S 2p in a) as prepared and b) AgSbS<sub>0.66</sub>Se<sub>1.34</sub> thin films.

#### **6.1.8 Morphological studies**

The surface morphologies of the samples are given in Figure 6.14. Uniformly distributed smaller spherical grains are observed for the sample heated 325 °C (Figure 6.14a). when the heating temperature is 325 °C the uniformly distributed smaller spherical grains are observed. When the temperature rises to 350 °C bigger grains with compact morphology can be seen from the Figure 6.14b. When the heating temperature increase to 375 °C, although the grains size is larger, some agglomeration can be seen on the surface. From the morphology, we can confirm that the heating temperature can encourage the grain growth and reduce grain boundary [161].



Figure 6.14 SEM images of  $AgSbS_{2-x}Se_x$  films heated at a) 325 °C ( $AgSbS_{0.84}Se_{1.16}$ ) b) 350 °C ( $AgSbS_{0.66}Se_{1.34}$ ) and c) 375 °C ( $AgSbS_{0.70}Se_{1.30}$ ).

# 6.1.9 Effect of heating conditions on optical properties

The measured absorbance, reflectance and transmittance spectra are given in Figure 6.15a-b. The absorption spectra show edge of absorption around 700-950 nm wavelength range. The absorption coefficient of the samples (350 °C and 375 °C) calculated from T and R. The absorption coefficient of each film is given in Figure 6.15c. All the films show high absorption coefficient of 10<sup>5</sup> cm<sup>-1</sup>. The bandgap of the films was calculated from Tauc plot and is given in the inset of Figure 6.15c. The calculated direct bandgap corresponding to 350 °C (AgSbS<sub>0.66</sub>Se<sub>1.34</sub>) and 375 °C (AgSbS<sub>0.70</sub>Se<sub>1.30</sub>) films are 1.42 eV and 1.44 eV respectively. The lowest bandgap value is observed for sample heated at 350 °C (AgSbS<sub>0.66</sub>Se<sub>1.34</sub>). The decrease in the bandgap can be due to a rise in Se content [161].


Figure 6.15 Reflectance and transmittance spectra b) absorption spectra and c) absorption coefficient vs energy, Tauc plot is given in the inset.

#### **6.1.10 Electrical properties**

The photocurrent for AgSbS<sub>2-x</sub>Se<sub>x</sub> films at different heating conditions is illustrated in Figure 6.16. The samples were illuminated with a halogen lamp and applied a bias voltage of 0.5 V. All the films exhibit photocurrent in the order of  $10^{-8}$  A. From the figure, an increase in dark current and photocurrent was observed when the heating temperature increased from 325 °C to 350 °C. The photosensitivity values are 150 %, 244 % and 200 % for samples heated at 325 °C, 350 °C and 375 °C respectively. The conductivity of the samples was calculated, and the values are  $3.3 \times 10^{-2}$ ,  $11 \times 10^{-2}$ ,  $7.6 \times 10^{-2}$  ( $\Omega$ cm)<sup>-1</sup>. The higher photosensitivity and conductivity value of the sample heated at 350 °C can be due to the higher crystallite size and compact morphology with reduced grain boundaries.



Figure 6.16 Photoresponse curve for  $AgSbS_{0.84}Se_{1.16}$ ,  $AgSbS_{0.66}Se_{1.34}$  and  $AgSbS_{0.70}Se_{1.30}$  films heated at 325 °C, 350 °C and 375 °C.

#### **6.1.11 Photovoltaic device**

Based on the above studies,  $AgSbS_{2-x}Se_x$  films formed at different heating conditions were used to fabricate solar cells with a CdS window layer. Sequentially deposited glass/FTO/CdS/Se-Ag-Sb<sub>2</sub>S<sub>3</sub> layers were heated at 350 °C and 375 °C to form the p-n junctions in the PV device. The J-V characteristics of the device are given in Figure 6.17, and the corresponding photovoltaic parameters in Table 6.2.



Figure 6.17 Evaluation of J-V characteristics of glass/FTO/CdS/AgSbS<sub>2-x</sub>Se<sub>x</sub>/C/Ag

|--|

SAMPLE	V <sub>oc</sub> (mV)	J <sub>sc</sub> (mA/cm <sup>2</sup> )	FF	Efficiency (η) %
AgSbS <sub>0.66</sub> Se <sub>1.34</sub> (350 °C)	465	12	0.44	2.5
AgSbS <sub>0.70</sub> Se <sub>1.30</sub> (375 °C)	445	11	0.42	2

The AgSbS<sub>0.66</sub>Se<sub>1.34</sub> (350 °C heated sample) absorber layer showed the best photovoltaic parameters such as  $V_{oc} = 465 \text{ mV}$ ,  $J_{sc} = 12 \text{ mA/cm}^2$ , and a conversion efficiency of 2.5 %. The improved  $J_{sc}$  and  $V_{oc}$  of 350 °C compared to 375 °C can be caused by the enhancement of crystallinity.

#### 6.1.12 Photodetector

 $FTO/CdS/AgSbS_{2-x}Se_x$  heterojunction selfpowered photodiodes (photovoltaic mode) were fabricated and the schematic diagram is given in Figure 6.18. Contacts were made using Ag paint. One contact was taken from the material and the other from FTO.



Figure 6.18 Schematic representation of photodetector in photovoltaic mode.

The device was fabricated in photovoltaic mode using p-type  $AgSbS_{2-x}Se_x$  film heated at 350 °C and n-type CdS deposited by chemical bath deposition. Figure 6.19a-b displays the cyclic photocurrent response of the fabricated device using LEDs (20 W) and solar simulator.



Figure 6.19 Photoresponse of the device (photovoltaic mode) illuminated with a) LEDs of wavelengths 465 (blue), 520 (green) and 590 nm (yellow) b) solar simulator (1000  $W/m^2$ ).

The sample showed a good response (photocurrent in the order of  $10^{-7}$  A) to different LEDs and solar simulator ( $10^{-4}$  A) without any bias voltage. The increase in photocurrent upon illumination without any bias voltage is because the inherent-built in potential arises from CdS/AgSbS<sub>2-x</sub>Se<sub>x</sub> interface act as the driving force to separate the electron-hole pairs which in turn increases the photocurrent [162]. Further, the device shows high stability and reproducibility when the illuminated light source was turned on-off alternatively during the measurements. The photosensitivity values towards different LEDs and solar simulator were calculated (section.4.2.5, Eq.15) and tabulated in Table 6.3.

Table 6.2 Sensitivity values of  $AgSbS_{2-x}Se_x$  self-powered photodiode using LEDs of different wavelength and solar simulator.

Source	Sensitivity (%)			
LED	Blue (465 nm)	784		
	Green (520 nm)	550		
	Yellow (590 nm)	224		
Solar simulator		1600		

The fabricated device performance was analyzed by calculating sensitivity, responsivity, detectivity and power law fitting. Calculations were done based on the response of the photodiode to laser wavelengths 532 and 785 nm. Photocurrent response of the photodiode with different laser powers (10-50 mW) and cyclic photoresponse at 50 mW corresponds to 532 and 785 nm lasers are given in Figure 6.20a-d.



Figure 6.20 Self-powered photodetection (photovoltaic mode) for 532 nm laser a) different powers and b) cyclic response, 785 nm laser c) different powers and d) cyclic response.

The fabricated photodiode shows very good response to 532 and 785 nm lasers without any bias voltage. The photocurrent is in the order of  $10^{-7}$  A and a slight improvement in the photocurrent value for photodiode illuminated with 532 nm lasers compared to 785 nm laser can be attributed to higher energy of the laser which improves the number of photogenerated electron-hole pairs [163]. The responsivity vs laser power density for 532 and 785 nm lasers are presented in Figure 6.21 a-b. The responsivity value depends on I<sub> $\lambda$ </sub>, intensity of the illumination source and the effective area of illumination of photodiode [164]. The higher responsivity of photodiode to 532 nm laser is due to the higher value I<sub> $\lambda$ </sub> and higher energy of the laser compared to 785 nm.



Figure 6.21 Plot of responsivity vs laser power density a)532 nm b)785 nm laser; (c,d) power law fitting of photocurrent vs incident power density.

Power law can be used to describe how photocurrent varies with illuminating light intensity (laser intensity) [165]. The power law relation is expressed in equation.

$$I_{ph} = CP^{\theta} \tag{22}$$

Where  $I_{ph}$  is the photocurrent, *C* is a constant for a particular wavelength, *P* is the power density and  $\theta$  determines the photocurrent response to incident power. The  $\theta$  value reflects the efficiency of photoexcited carriers [166]. The fitting curve with  $\theta = 0.94$  and 0.95 is obtained, which is close to the ideal value '1', suggesting very few trap states in the bandgap and also good quality CdS/AgSbS<sub>2-x</sub>Se<sub>x</sub> self-powered photodiodes [167]. Additionally, the detectivity of the photodiode was also calculated, which determines the ability to detect the weak optical signal [167]. The detectivity is given by,

$$D = \frac{RA^{1/2}}{(2eI_{dark})^{1/2}}$$
(23)

Where *R* is the responsivity, A is the effective area of illumination, e is the charge of an electron and  $I_{dark}$  is the dark current. The sensitivity, responsivity and detectivity values of the self-powered photodiode for different laser powers (532 and 785 nm lasers) are tabulated below.

Table 6.3 Sensitivity, responsivity and detectivity of  $AgSbS_{2-x}Se_x$  photodiode illuminated with 532 and 785 nm lasers of different powers.

Laser (nm)	Laser power (mW)	Sensitivity (%)	Responsivity (AW <sup>-1</sup> ), 10 <sup>-6</sup>	Detectivity (Jones), 10 <sup>9</sup>
	10	40	6.35	5.90
532	20	70	5.75	5.85
	30	88	5.69	5.47
	40	247	5.67	5.63
	50	411	5.56	5.37
	10	35	1.40	2
785	20	45	1.27	1.95
	30	60	1.20	1.92
	40	116	1.14	1.98
	50	211	1.01	1.89

To show the wide spectral range, we also measured the photoresponse of the self-powered photodiode using 405 (50 mW), 840 (100 mW) nm and 1064 nm (939 mW) lasers.



Figure 6.22 Self-powered photodetection (photovoltaic mode) for lasers (405 nm, 840 nm and 1064 nm) at zero bias.

Figure 6.23 represents laser wavelength vs photocurrent graph for different lasers. The graph shows that high photocurrent is observed for 532 nm laser source.



Figure 6.23 Wavelength vs photocurrent for different lasers.

We also fabricated self-powered photodiodes (photoconductive mode) of CdS/AgSbS<sub>2-x</sub>Se<sub>x</sub> heterojunctions with AgSbS<sub>2-x</sub>Se<sub>x</sub> heated at 350 and 375° C. The schematic representation of the photodiode in photoconductive mode is represented in figure below. Ag electrodes with  $7 \times 7$  dimension was painted over the surface.



Figure 6.24 CdS/AgSbS<sub>2-x</sub>Se<sub>x</sub> in photoconductive mode.

The photocurrent response of the self-powered photodiodes are examined using LEDs of different wavelengths, 532 and 785 nm continuous lasers with different powers and 405 and 840 nm diode lasers. The cyclic photocurrent response of the photodiodes recorded using LEDs with an on-off interval of 10 s for 5 cycles is given in Figure 6.25a-b. A fast, consistent, and repeatable photocurrent was observed throughout the cycles.



Figure 6.25 Photocurrent response of self-powered photodiodes (photoconductive mode) to different LEDs a) 350 °C (AgSbS<sub>0.66</sub>Se<sub>1.34</sub>) b) 375 °C (AgSbS<sub>0.70</sub>Se<sub>1.30</sub>) heated samples.

Figure 6.26 a-d represents the photocurrent response of the fabricated photodiode illuminated with 532 and 785 nm lasers with no bias. The laser power was varied from 10 to 50 mW by multiples of 10. The self-powered photodiode shows photocurrent in the order of  $10^{-7}$  A under the illumination of 532 and 785 nm lasers. Photocurrent increases linearly with an increase in the laser powers from 10 to 50 mW. The photodiode with AgSbS<sub>2-x</sub>Se<sub>x</sub> heated at 350 °C shows a high photocurrent compared to 375. This is due to the better crystallinity and higher grain size of the material. The stability and reproducibility of the photodiode were confirmed by the cyclic response measurements presented in Figure 6.26e-h. The photocurrent increases and then returns to a low photocurrent value when the light is alternatively turned on and off. The photocurrent of 532 nm laser source is ~10 times greater than 785 nm laser source for 350 °C heated sample. This improvement in photocurrent can be related to the proportionality between number of the excited carriers and the energy of laser source or excitation source for a fixed source power (50 mW) [168].





Figure 6.26 Photoresponse of photodiode (photoconductive mode) (AgSbS<sub>2-x</sub>Se<sub>x</sub> heated at 350 °C and 375 °C) with different laser powers (a,b) 532 nm laser, (c,d) 785 nm laser, cyclic response to (e,d) 532 nm ,(g,h) 785 nm lasers.

The photodiode parameters such as sensitivity and responsivity were calculated. The plot of sensitivity versus laser power density for 532 and 785 nm lasers for the self-powered photodiode is indicated in Figure 6.27a-b.



Figure 6.27 Sensitivity vs laser power density plot for photodiodes (photoconductive mode) with a) 532 b) 785 nm lasers.



Figure 6.28 Responsivity vs power density plot for photodiodes (photoconductive mode) with a) 532 and b) 785 nm laser.

The responsivity gives the amount of photocurrent generated per unit area per unit illumination intensity. The responsivity plot for different power densities is given in Figure 6.28a-b. The highest value of responsivity was observed for the photodiode fabricated with AgSbS<sub>0.66</sub>Se<sub>1.34</sub> film. The higher value of I<sub> $\lambda$ </sub>, which is the difference between photocurrent and dark current could be the reason for higher value of responsivity and sensitivity value in 350 °C sample compared to 375 °C sample.

There have been numerous reports of self-powered photodetectors based on p-n heterojunction in recent years. Due to the presence of two or more materials with different bandgaps a p-n heterojunction can provide better light absorption leading to an enhanced device performance [169,170]. The built-in potential developed at the p-n heterojunction act as the driving force which inhibit the recombination of photogenerated carriers. The outcome is a photovoltaic current due to the migration of electrons to conduction band and holes to valence band. Photoelectric effect is the basic principle of light detection in self-powered photodetectors. Sensitivity and responsivity are two important parameters that defines the performance of a self-powered photodetector. Our fabricated device has obtained a maximum sensitivity of 2000 % and responsivity  $9.5 \times 10^{-6}$  (AW)<sup>-1</sup>.

#### 6.1.13 Graphene incorporated AgSbS<sub>2-x</sub>Se<sub>x</sub> thin films

The XRD patterns of graphene incorporated  $AgSbS_{2-x}Se_x$  thin films formed under different amounts of graphene (1, 3 and 5 mg) are given in Figure 6.29. Three peaks are observed in all the samples. The sample with 1 mg graphene (AgSbSSe+G1) has peaks at 26.73°, 31.20° and 44.65° corresponds to (111), (200) and (220) planes of AgSbS<sub>2-x</sub>Se<sub>x</sub>, confirmed by comparing the peak position with AgSbS<sub>2</sub> and AgSbSe<sub>2</sub>. When the graphene amount increased to 3 and 5 mg peak intensity corresponding to (111) plane also incresed. The peak position is observed at 26.48°, 31° and 44.60°. The normalized peak of (200) is given in the inset, which indicates that as the amount of graphene increases the compound becomes more Se rich and it shows more shift towards cubic AgSbSe<sub>2</sub>. The calculated x values are 1.65, 1.70 and 1.80 and the corresponding composition AgSbS<sub>0.40</sub>Se<sub>1.60</sub>, AgSbS<sub>0.30</sub>Se<sub>1.70</sub>, and AgSbS<sub>0.20</sub>Se<sub>1.80</sub>. The calculated crystallite size values are 28, 31 and 33 nm. We can observe an improvement in the crystallite size with the graphene amount. The improvement in peak intensity and crystallite size confirm the improved crystallinity of the films due to graphene incorporation. Moreover, enhancement in crystallinity with graphene in CZTS was reported previously [171]. The incorporated graphene act as crystalline sites(seed) for the growth of AgSbS<sub>2-x</sub>Se<sub>x</sub> structure and thereby improved the crystallinity. Further, increase in XRD peak intensity with GO amount in CZTS was reported by Renuka V. Digraskar also supports our results [172].



Figure 6.29 XRD patterns of AgSbS<sub>2-x</sub>Se<sub>x</sub>:Graphene films.

The Raman spectra of the AgSbS<sub>2-x</sub>Se<sub>x</sub>:Graphene films are presented in Figure 6.30. From the figure, we can see that broad peaks are detected at wavenumbers 186 and 261 cm<sup>-1</sup> in AgSbS<sub>2-x</sub>Se<sub>x</sub>:Graphene thin films. Not many reports are available in the literature regarding this material. However, in a recent report on local structural distortion and the respective phonon dispersion analysis of pure AgSbSe<sub>2</sub> [173], broadening of the vibrational peaks (195 and 215 cm<sup>-1</sup>) has been mentioned. Comparing with the pure AgSbSe<sub>2</sub> data (215 cm<sup>-1</sup>), we can see that the Raman peaks are shifted to higher frequency (261 cm<sup>-1</sup>) due to sulfur incorporation and broadened due to the local symmetry breaking causing the structural distortion. Along with these peaks G and 2D bands of graphene is also present in the spectra which confirms the incorporated graphene into AgSbS<sub>2-x</sub>Se<sub>x</sub> films. G and 2D band intensity ratio confirms that incorporated graphene is multilayer in nature.



Figure 6.30 Raman spectra of AgSbS<sub>0.40</sub>Se<sub>1.60</sub>, AgSbS<sub>0.30</sub>Se<sub>1.70</sub> and AgSbS<sub>0.20</sub>Se<sub>1.80</sub> thin films.

#### **6.1.14** Chemical state

A comparative study of XPS high resolution spectra of AgSbS<sub>2-x</sub>Se<sub>x</sub>:Graphene thin films with different graphene amounts are given in Figure 6.31. Ag 3d, Sb 3d, S 2p, Se 3d and C 1s peaks in AgSSSe+G1, AgSbSSe+G3 and AgSbSSe+G5 thin films are presented in Figure 6.31a-o. Ag 3d<sub>5/2</sub> and Ag 3d<sub>3/2</sub> peaks have almost same intensity in all the samples (Figure 6.31a-c). Sb 3d doublets are shown in Figure 6.31d-e, where the dominant Sb 3d<sub>5/2</sub> and Sb 3d<sub>3/2</sub> binding energies correspond to the Sb<sup>3+</sup> state. Peaks marked as I and II corresponds to metallic Sb (Sb<sup>0</sup>). Sb 3d peak intensity increases from AgSSSe+G1 to AgSbSSe+G5. Comparing the S 2p (Figure 6.31g-i) peak, the intensity reduces from AgSSSe+G1 to AgSbSSe+G5. In the same region another doublet peak of Se 3p<sub>3/2</sub> and Se 3p<sub>1/2</sub> is present, and the intensity of these peaks increases from AgSSSe+G1 to AgSbSSe+G5. In addition, peak intensity of Se 3d also increases with the graphene amount in the samples, all these results are in correlation with our XRD results. The C 1s spectra is presented in Figure 6.31m-o. The two peaks at 284.64 eV and 285.47 eV corresponds to sp<sup>2</sup> and sp<sup>3</sup> hybridized C.

From the atomic percentage value obtained from XPS analysis, Se/S ratio was calculated in each sample, and the obtained values are 1.83, 2.45 and 2.60 for AgSSSe+G1

(AgSbS $_{0.40}$ Se $_{1.60}$ ), AgSbSSe+G3 (AgSbS $_{0.30}$ Se $_{1.70}$ ) and AgSbSSe+G5 (AgSbS $_{0.20}$ Se $_{1.80}$ ) respectively. Se/S ratio increases with graphene amount, this is in accordance with our XRD results.





Figure 6.31 XPS high resolution spectra of (a-c) Ag 3d, (d-f) Sb 3d, (g-i) S 2p, (j-l) Se 3d and (m-o) C 1s in AgSSSe+G1, AgSbSSe+G3 and AgSbSSe+G5.

## 6.1.15 Morphology of AgSbS<sub>2-x</sub>Se<sub>x</sub>:Gr thin films

The morphological studies of the graphene incorporated AgSbS<sub>2-x</sub>Se<sub>x</sub> films are shown in Figure 6.32a-c. The AgSbSSe+G1 film shows dense and uniformly distributed smaller grains on the surface. The uniformly distributed large spherical grains along with the layered structure of graphene is clearly seen on the surface of AgSbSSe+G3 and AgSbSSe+G5 films (Figure 6.32b-c). The SEM also shows improvement in grain size with graphene amount which is in accordance with XRD results.



Figure 6.32 SEM images of a) AgSSSe+G1 ( $AgSbS_{0.40}Se_{1.60}$ ) b) AgSbSSe+G3 ( $AgSbS_{0.30}Se_{1.70}$ ) and c) AgSbSSe+G5 ( $AgSbS_{0.20}Se_{1.80}$ ).

#### 6.1.16 Optical properties of AgSbS2-xSex:Graphene thin films

The optical transmittance and reflectance spectra, absorption spectra and Tauc plot of the three thin films are presented in Figure 6.33. Improvement in the optical absorption was observed for samples with increasing the graphene content. The transmittance and reflectance spectra are illustrated in Figure 6.33a. The bandgap values of the samples were estimated from Tauc plot, the calculations have already been discussed. According to Figure 6.33c, the bandgap value decreases from 1.44 eV to 1.23 eV as the graphene amount increase. The decrease in bandgap with graphene amount can be attributed to the change in composition or increase in the Se amount as observed from the XRD, compared to AgSbSSe+G1 samples, AgSbSSe+G3 and AgSbSSe+G5 samples are rich in selenium, or they are completely converted into pure selenides. Moreover, an increase in crystallinity also contribute to the reduction in bandgap.



Figure 6.33 a) Transmittance and reflectance b) absorption spectra and c) Tauc plots of AgSbSSe+G1(AgSbS $_{0.40}$ Se $_{1.60}$ ), AgSbSSe+G3 (AgSbS $_{0.30}$ Se $_{1.70}$ ) and AgSbSSe+G5 (AgSbS $_{0.20}$ Se $_{1.80}$ ) thin films.

## 6.1.17 Studies on electrical properties of AgSbS2-xSex:Graphene thin films

The electrical properties of the films were studied by measuring the photocurrent response. The samples were illuminated with halogen lamp (50 W) with a bias voltage of 0.5 V and the corresponding photoresponse curve is given in Figure 6.34. The samples show photocurrent in the order of  $10^{-7}$  A. The enhancement in photocurrent value was observed when graphene amount was increased from 1 to 5 mg. Improvement in photocurrent upon

incorporation of graphene has been reported in many articles [174–177]. Recently, graphene incorporated SnS films demonstrated increase in the photocurrent compared to pure SnS films. Similarly, Dalio Shao et.al also reported photocurrent enhancement in ZnO-graphene photodetectors. Under illumination AgSbS<sub>2-x</sub>Se<sub>x</sub> film behave like a light harvesting medium. The main contribution to light absorption is from AgSbS<sub>2-x</sub>Se<sub>x</sub> films. The photogenerated charge carriers are transferred from AgSbS<sub>2-x</sub>Se<sub>x</sub> layer to graphene layer. Since graphene has high carrier mobility it accumulates fewer electrons, improving carrier transport and leading to an improvement in photocurrent. When the illumination is turned off, the photogenerated carriers move to AgSbS<sub>2-x</sub>Se<sub>x</sub> and they recombine with the holes leading to photocurrent decay. Moreover, graphene can act as an electron shuttle to induce electron transfer from conduction band of AgSbS<sub>2-x</sub>Se<sub>x</sub> resulting in efficient charge carriers separation and substantial amendment in the photocurrent [172]. The calculated photosensitivity and conductivity was observed for AgSbSse+G5 film.



Figure 6.34 Photocurrent response of AgSbSSe+G1 (AgSbS<sub>0.40</sub>Se<sub>1.60</sub>), AgSbSSe+G3 (AgSbS<sub>0.30</sub>Se<sub>1.70</sub>) and AgSbSSe+G5 (AgSbS<sub>0.20</sub>Se<sub>1.80</sub>) thin films.

#### 6.1.18 Photovoltaic device

The AgSbS<sub>2-x</sub>Se<sub>x</sub>:Graphene thin films were incorporated into solar cells as an absorber layer. Glass/FTO/n-CdS /p-AgSbS<sub>2-x</sub>Se<sub>x</sub>:Graphene/C/Ag was the basic structure of

fabricated solar cells. The schematic of the solar cell structure and the J-V plots obtained after illumination (1000 W/cm<sup>2</sup>) with AgSbSSe+G1, AgSbSSe+G3 and AgSbSSe+G5 absorber layers is displayed in Figure 6.35a-b. The photovoltaic parameters of each solar cells are given in Table 6.5. The best solar cell efficiency value of 3.5% was obtained for solar cells with AgSbSSe+G5 as the absorber layer. The efficiency obtained without graphene was 2.5%, that is already discussed. We can see that the efficiency increased from 2.5 to 3.5% upon incorporation of graphene into AgSbS<sub>2-x</sub>Se<sub>x</sub> thin films. In addition, the J<sub>sc</sub> and FF also increased from 12 mA/cm<sup>2</sup>, 44% to 14 mA/cm<sup>2</sup>, 57%. To study the effect of graphene incorporated AgSbS<sub>2-x</sub>Se<sub>x</sub> absorber layer (AgSbSSe+G7 and AgSbSSe+G10).



Figure 6.35 a) schematic of solar cells b) J-V plots of Glass/FTO/CdS /p-AgSbS<sub>2-x</sub>Se<sub>x</sub>/C/Ag

Sample	V <sub>oc</sub> (mV)	Jsc	FF	Efficiency
		(mA/cm <sup>2</sup> )		(ŋ) %
AgSbSSe+1 (AgSbS <sub>0.40</sub> Se <sub>1.60</sub> )	465	12	0.50	2.7
AgSbSSe+3 (AgSbS <sub>0.30</sub> Se <sub>1.70</sub> )	425	13	0.54	3
AgSbSSe+5 (AgSbS0.20Se1.80)	445	14	0.57	3.5
AgSbSSe+7 (AgSbS0.17Se1.83)	405	20	0.30	2.4
AgSbSSe+10 (AgSbS0.15Se1.85)	324	27	0.31	2.7

Table 6.4 Photovoltaic parameters of AgSbS<sub>2-x</sub>Se<sub>x</sub>:Graphene solar cells.

Graphene has a work function of 4.8 eV which matches with the valence band of AgSbS<sub>2-x</sub>Se<sub>x</sub> for hole extraction [177,178]. The improvement in efficiency with graphene incorporation is due to the presence of highly conductive graphene layer as a back electrode which enhances the extraction of holes. In addition, reduction of barrier height with AgSbS<sub>2-x</sub>Se<sub>x</sub> layer also helps in faster collection of holes and reducing the recombination thus enhancing the solar cell performance [179,180]. We can see from the table that the solar cell efficiency increased from 2.7 to 3.5 % when the graphene amount was increased from 1 to 5 mg. The improvement can be due to the enhancement in the crystallinity of AgSbS<sub>2-x</sub>Se<sub>x</sub> layer as observed from XRD and SEM. The improvement in crystalline quality or increased crystallite size and less grain boundaries decreases the recombination hence better solar cell performance [171]. The efficiency decreased when the graphene amount was further increased to 7 and 10 mg. The reduction can be attributed to an increase in the series resistance as observed from the J-V plot.

#### 6.1.19 Self-powered photodetectors

The above studies indicate the fabricated device has high built-in electric field so it can act as a photodiode to detect different wavelengths of light without any power consumption. FTO/CdS/AgSbS<sub>2-x</sub>Se<sub>x</sub>:Graphene photodiode was fabricated in photovoltaic mode as shown Figure 6.36. The photodiodes were irradiated with LEDs of different wavelengths (465 (blue), 520 (green) and 590 nm (yellow)) without any bias voltage. Under the illumination high photocurrent was observed for all the device, which increases with a decrease in the wavelength of LEDs. The variation of photocurrent under different wavelengths of LEDs demonstrates that the CdS/AgSbS<sub>2-x</sub>Se<sub>x</sub>:Graphene photodiodes have good photoresponse properties at visible region without applying any bias voltage. The cyclic photocurrent response under LEDs confirms the stability and reproducibility of the fabricated devices. The calculated sensitivity values are tabulated in Table 6.6.



Figure 6.36 Schematic illustration of CdS/AgSbS<sub>2-x</sub>Se<sub>x</sub>:Graphene self-powered photodiode (photovoltaic mode).



Figure 6.37 Photocurrent response of photodiodes (photovoltaic mode) fabricated with AgSbSSe+G1 (AgSbS<sub>0.40</sub>Se<sub>1.60</sub>), AgSbSSe+G3 (AgSbS<sub>0.30</sub>Se<sub>1.70</sub>) and AgSbSSe+G5 (AgSbS<sub>0.20</sub>Se<sub>1.80</sub>) thin films.

Sample	LEDs	Sensitivity (%)
AgSbSSe+G1	Blue	2100
(AgSbS0.40Se1.60)	Green	1600
	Yellow	1200
AgSbSSe+G3 (AgSbS0.30Se1.70)	Blue	3150
	Green	1830
	Yellow	1300
AgSbSSe+G5 (AgSbS0.20Se1.80)	Blue	3233
	Green	2515
	Yellow	1656

Table 6.5 Sensitivity values of FTO/CdS/AgSbS<sub>2-x</sub>Se<sub>x</sub>:Graphene photodiodes.

We further analyzed the photoresponse of CdS/AgSbS<sub>2-x</sub>Se<sub>x</sub>:Graphene photodiodes using continuous lasers of wavelength 532 and 785 nm with varying laser powers (10, 20, 30, 40 and 50 mW). The response of AgSbSSe+G1, AgSbSSe+G3 and AgSbSSe+G5 based photodiodes without any bias voltage corresponding to 532 and 785 nm lasers is shown in Figure 6.38 and Figure 6.39 respectively. The device showed good response to both the lasers. The highest photocurrent of 10<sup>-5</sup> A was obtained for the photodiode with AgSbSSe+G5, which is 20 times higher than the photodiodes of pure AgSbS<sub>2-x</sub>Se<sub>x</sub> without graphene layer (already discussed in section 6.1.12). The presence of graphene helps for the smooth transfer of charge carriers which are separated by the built-in electric field present at the heterojunction in self powered photodiodes [170,181,182]. The enhancement in the photocurrent with laser powers results from the fact that the number of photogenerated carriers increases with higher laser powers, these carriers are transferred to the electrode through graphene which acts as shuttle for the transfer of carriers. In addition, the photocurrent increases (decreases) when the light is turned on (off). The response under the illumination of multiple cycles is also shown in Figure 6.38d-e and 6.39d-e. A stable and repeatable response is observed for the CdS/AgSbS<sub>2-x</sub>Se<sub>x</sub>:Graphene photodiodes throughout cycles. It suggests that CdS/AgSbS<sub>2-x</sub>Se<sub>x</sub>:Graphene heterojunction can act as a good quality photodiode under operation without any bias voltage.



Figure 6.38 The photocurrent response of photodiodes (photovoltaic mode) under 532 nm laser with different laser powers and the corresponding cyclic measurements (50 mW) (a and b) AgSbSSe+G1 (AgSbS<sub>0.40</sub>Se<sub>1.60</sub>), (c and d) AgSbSSe+G3 (AgSbS<sub>0.30</sub>Se<sub>1.70</sub>), (e and f) AgSbSSe+G5 (AgSbS<sub>0.20</sub>Se<sub>1.80</sub>).



Figure 6.39 The photocurrent response of photodiodes (photovoltaic mode) under 785 nm laser with different laser powers and the corresponding cyclic measurements (50 mW) (a and b) AgSbSSe+G1 (AgSbS<sub>0.40</sub>Se<sub>1.60</sub>), (c and d) AgSbSSe+G3 (AgSbS<sub>0.30</sub>Se<sub>1.70</sub>), (e and f) AgSbSSe+G5 (AgSbS<sub>0.20</sub>Se<sub>1.80</sub>).

The sensitivity of the device to 532 and 785 nm lasers with different powers was calculated using the Eq.15 (section 4.2.5). The plot of sensitivity vs laser power density is presented in Figure 6.40. The device shows good sensitivity towards different lasers and different power densities. Further, the influence of laser power density on the device was determined using responsivity calculations. The responsivity vs laser power density plots for 532 and 735 nm lasers are displayed in Figure 6.40a-b. The decrease in responsivity with an increase in laser power density may be due to enhanced scattering or recombination at higher power density [181].



Figure 6.40 Sensitivity of CdS/AgSbS<sub>2-x</sub>Se<sub>x</sub>:Graphene photodiodes (photovoltaic mode) towards different laser powers a) 532 nm b) 785 nm.



Figure 6.41 Responsivity of CdS/AgSbS<sub>2-x</sub>Se<sub>x</sub>:Graphene photodiodes (photovoltaic mode) towards different laser powers a) 532 nm b) 785 nm.

To examine the wide spectral range of the fabricated photodiode we measured the response corresponding to laser diodes of wavelength 405 (50 mW), 840 (100mW) nm and 1064 nm (939 mW) without any bias voltage. The CdS/AgSbS<sub>2-x</sub>Se<sub>x</sub>:Graphene photodiodes responded well to both the lasers as shown in Figure 6.42.



Figure 6.42 Photoresponse of the  $CdS/AgSbS_{2-x}Se_x$ :Graphene photodiodes (photovoltaic mode) to a) 405 nm b) 840 nm lasers c) 1064 nm without any bias voltage.

To study the dependence of sensitivity with wavelength of laser source we plotted a graph between sensitivity vs wavelength and is given in the Figure 6.43. From the plot, highest value of sensitivity is observed for the diode under the illumination of 532 nm laser source.



Figure 6.43 Sensitivity vs wavelength for CdS/AgSbSSe+G5 photodiode.

In conclusion, we synthesized Se nanocolloids by laser irradiation technique and it was spin coated on glass/Sb<sub>2</sub>S<sub>3</sub>-Ag precursor layers and studied the effect of Se content and heating temperature on structural, morphological, optical, and electrical properties of AgSbS<sub>2-x</sub>Se<sub>x</sub>. The best solar cell device fabricated using AgSbS<sub>0.66</sub>Se<sub>1.34</sub> absorber showed an efficiency of 2.5%. Self-powered photodetectors fabricated in photovoltaic as well as photoconductive mode presented stable photodetection properties over a wide range of wavelengths (UV-Vis-NIR) region. The highest sensitivity (2000%) and responsivity (9.5×10<sup>-6</sup> AW<sup>-1</sup>) was obtained for AgSbS<sub>0.66</sub>Se<sub>1.34</sub> based photodetector in photoconductive mode with 532 nm laser illumination. Further to improve the properties of the AgSbS<sub>2-x</sub>Se<sub>x</sub> thin films graphene was incorporated. An increase in photocurrent and conductivity was observed for AgSbS<sub>0.20</sub>Se<sub>1.80</sub>:Graphene thin films. In addition, the solar cell efficiency increased from 2.5 were detection of graphene. Fabricated photodetectors showed detection

up to 1064 nm wavelength without any power consumption. The photodetectors showed better performance with high responsivity  $(9.5 \times 10^{-6} \text{ (AW}^{-1}) \text{ and sensitivity (2000\%)})$ .

# CHAPTER 7 GENERAL CONCLUSIONS AND OUTLOOK

In summary,

- A systematic study on AgSbS<sub>2</sub> and AgSbS<sub>2-x</sub>Se<sub>x</sub> thin films with x varies from 0.58 to 1.34. We were able to successfully fabricate solar cells and photodetectors from these materials with better performances.
- Monoclinic AgSbS<sub>2</sub> thin films were fabricated by heating glass/Sb<sub>2</sub>S<sub>3</sub>-Ag layers with different silver thickness. Their structure, composition, morphology, and optoelectronic properties were influenced by the silver layer thicknesses. The optical bandgap value was found to be in the range of 1.7-1.8 eV. The photovoltaic device fabricated with AgSbS<sub>2</sub> absorber and CdS window layer showed good photovoltaic performance with a calculated efficiency 1.5 %, the highest efficiency ever reported for CdS/AgSbS<sub>2</sub> junction based solar cells.
- → We synthesized AgSbS<sub>2-x</sub>Se<sub>x</sub> thin films by heating glass/Sb<sub>2</sub>S<sub>3</sub>-Ag<sub>2</sub>Se layer. A systematic control of Se/S ratio was achieved and thus, we obtained the solid solution thin films with stoichiometric formulas AgSbS<sub>1.42</sub>Se<sub>0.58</sub>, AgSbS<sub>1.38</sub>Se<sub>0.62</sub>, AgSbS<sub>1.36</sub>Se<sub>0.64</sub>, AgSbS<sub>1.28</sub>Se<sub>0.72</sub>, AgSbS<sub>1.24</sub>Se<sub>0.78</sub> and AgSbS<sub>1.16</sub>Se<sub>0.84</sub> as determined from XRD. The structural, opto-electronic properties, morphology and composition were studied using different techniques. The optical bandgap obtained for the films is in the range 1.45-1.60 eV, suitable for photovoltaic application. The best device with configuration Glass/FTO/CdS/AgSbS<sub>2-x</sub>Se<sub>x</sub>/C/Ag produced: V<sub>oc</sub> = 525 mV, a J<sub>sc</sub> = 15 mA/cm<sup>2</sup>, FF=0.53 and  $\eta = 4.2$  %, using AgSbS<sub>1.28</sub>Se<sub>0.72</sub> thin films.
- ➤ We explored the capability of  $AgSbS_{2-x}Se_x$  (x = 0.34 to 0.72) as a photodetector for the first time. The fabricated photodetector in photoconductive and self-powered mode showed a wide spectral range of detection (405-1064 nm) with good photodetector parameters of sensitivity and responsivity.
- Selenium rich AgSbS<sub>2-x</sub>Se<sub>x</sub> thin films were prepared by heating (at various temperatures) the precursor layer formed by the spin coating of Se nancolloid on glass/Sb<sub>2</sub>S<sub>3</sub>-Ag layer. We found that the bandgap values and electrical properties

were tunable by changing Se to S ratio in the films. The photovoltaic device developed from these materials displayed a maximum efficiency of 2.5%. These materials were also explored for self-powered photodetector (photovoltaic and photoconductive mode) application and demonstrated detection sensitivity in a broad range of wavelengths (UV-VIS-NIR) and good stability for wireless or remote sensing without any power usage.

- AgSbS<sub>2-x</sub>Se<sub>x</sub>:Graphene thin films exhibited an improvement in opto-electric properties compared to pure films. PV device fabricated using AgSbS<sub>0.20</sub>Se<sub>1.80</sub>:Graphene absorber layer showed an efficiency of 3.5%. A selfpowered photodiode in photoconductive mode showed high sensitivity and responsivity values up to 1064 nm wavelength range.
- The optoelectronic properties and best device performance of AgSbS<sub>2-x</sub>Se<sub>x</sub> thin films prepared by different methods is given in the table below.

Sample	Bandgap (Eg)	Sensitivity	Photovoltaic device
	eV	%	efficiency (η)
			%
AgSbS <sub>1.28</sub> Se <sub>0.72</sub>	1.55	202	4.2
AgSbS <sub>0.66</sub> Se <sub>1.34</sub>	1.42	244	2.5
AgSbS <sub>0.20</sub> Se <sub>1.80</sub>	1.23	190	3.5

- ➤ The geometry structure, band structure and density of states of the monoclinic AgSbS<sub>2</sub> were investigated under the framework of density functional theory. Monoclinic AgSbS<sub>2</sub> exhibited a bandgap of 1.77 eV in correlation with our experimental value. SCAPS-1D calculations were done for AgSbS<sub>2-x</sub>Se<sub>x</sub> solar cells and we obtained a maximum efficiency value of 17.5% corresponding to 1µm thickness and 1.2 eV bandgap. The SCAPS results imply the scope of AgSbS<sub>2-x</sub>Se<sub>x</sub> material to produce high efficiency solar cells by controlling the Se/S ratio at optimum thin film growth conditions.
- From all the results we explained in this thesis we conclude that the proposed hypothesis has been fulfilled.

In general, this study provides a clear knowledge regarding the structure, morphology, and optoelectronic properties of emerging metal chalcogenides such as AgSbS<sub>2</sub> and AgSbS<sub>2-x</sub>Se<sub>x</sub>

for photovoltaic and opto-electronic applications. This study also indicates that the optoelectric properties of these materials can be varied by changing material composition. This research can provide a new path for the fabrication of photovoltaic devices with earth abundant, less toxic and cost-effective thin films.

# **SCOPE OF THE WORK**

Silver antimony sulfoselenide is an emerging photovoltaic material with earth abundant and less toxic elements with tunable opto-electric properties suitable for photovoltaic and optoelectronic applications. Our experimental results show a stable and reproducible photovoltaic performance and photodetector parameters. In addition, the simulation results using SCAPS-1D demonstrates that there is a lot of room to improve the device efficiency. Overall, this research work shows the scope of this material, and it can encourage the scientific community to work on these materials to produce devices with high performance.

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