

**STUDIES ON PREPARATION AND
CHARACTERISATION OF SPRAY DEPOSITED
ANTIMONY TRISULPHIDE AND ANTIMONY
TRISELENIDE THIN FILMS AND THEIR USE IN
STORAGE CELLS**

**A THESIS SUBMITTED TO
SHIVAJI UNIVERSITY, KOLHAPUR**

**FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY**

IN

PHYSICS

UNDER THE FACULTY OF

SCIENCE

BY

Mr. K.Y. RAJPURE

M.Sc.

UNDER THE GUIDANCE OF

Dr. C.H. BHOSALE

M.Sc. Ph.D.

**DEPARTMENT OF PHYSICS
SHIVAJI UNIVERSITY, KOLHAPUR – 416004**

1999

DECLARATION

I hereby declare that the thesis entitled “STUDIES ON PREPARATION AND CHARACTERISATION OF SPRAY DEPOSITED ANTIMONY TRISULPHIDE AND ANTIMONY TRISELENIDE THIN FILMS AND THEIR USE IN STORAGE CELLS” completed and written by me has not previously formed the basis for the award of any Degree or Diploma or similar title of this or any other University or examining body.

Research Student

(K. Y. RAJPURE)

PLACE : KOLHAPUR

DATE :

CERTIFICATE

This is to certify that the thesis entitled “STUDIES ON PREPARATION AND CHARACTERISATION OF SPRAY DEPOSITED ANTIMONY TRISULPHIDE AND ANTIMONY TRISELENIDE THIN FILMS AND THEIR USE IN STORAGE CELLS” which is being submitted herewith for the award of Degree of Doctor of Philosophy in Physics of Shivaji University, Kolhapur is the result of the original research work completed by Shri. K.Y. Rajpure under my supervision and guidance and to the best of my knowledge and belief the work embodied in this thesis has not formed earlier the basis for the award of any degree or similar title of this or any other University or examining body.

Research Guide
Dr. C.H. Bhosale
Reader,
Department of Physics,
Shivaji University, Kolhapur -416004

PLACE : Kolhapur
DATE :

A C K N O W L E D G E M E N T S

I have great pleasure in expressing my deep sense of indebtedness and heartfelt gratitude to Dr. C.H. Bhosale, Reader, Department of Physics, Shivaji University, Kolhapur for his expert and valuable guidance and continuous encouragement given to me during the course of work.

I am highly grateful to Prof. K.L.Narayana, Head, Department of Physics, Shivaji University, Kolhapur for making me available the laboratory facilities. My deep appreciations are due to Prof. S.H.Pawar, Former Head. of Physics department for his interest and encouragement, which helped me a lot.

I am indebted to Dr. C.D.Lokhande, Dr.P.S. Patil and Dr. M.D.Uplane for fruitful discussions and valuable suggestions during the course of the work.

I wish to express my appreciation to Dr. P. B. Wagh, my senior colleague and a real friend; for his co-operation, love and homely behavior given to me in every moment of this work.

I am thankful to Messers V.V. Killedar, A.P. Torane, N. S. Gaikwad, S. R. Gadakh, L.D. Kadam, S.J. Lade, R. S. Mane, B. R. Sankpal, S.D. Sartale, J. V. Thorat, A. M. Patil, B. J. Lokhande and the members of our Thin Film Physics group as a whole for their assistance in experimental work and discussions.

I sincerely appreciate the help rendered by Mr. D. Haranath, Mr. D.S. Mali, Mrs. N..V. Desai, Mrs. L.A. Ekal, Mr. Dilip Shivgan, Mr. A.L. Dhebe, Mr. S. M. Bamane, Mr. U. L. Shinde, Mr. P. V. Bansode, Mr. B. V. Sakhare, Miss. P. A. Anarase, Mr. M.N. Kusumade, S.S. Kumbhar and V.L. Mathe.

I am thankful to all my teachers as well as administrative, laboratory and work shop staff of the Physics department and CFC, USIC staff for their co-operation.

It is my solemn duty to thank Principal D. B. Mahanwar of Principal D. B. Bhosale College of Koregaon (Dist. Satara) for continuous encouragement and timely suggestions during the course of my work.

I am deeply indebted to the DST (Department of Science and Technology) , Govt. of India, New Delhi, for the award of two year Junior Research Fellowship and one year Senior Research Fellowship to pursue this work.

I express deep sense of love to my brother-in-law Shri. Sadashiv Shirke, Khandala (Dist. Satara), who is the chief source of my inspiration. At the same time, the sense of tolerance and greater patience showed by my brother Balasaheb is enormously admirable. I would like to remember my loving Mother and Late. Father and other family members whose good will and inspiration far exceeds what the words of appreciation can express.

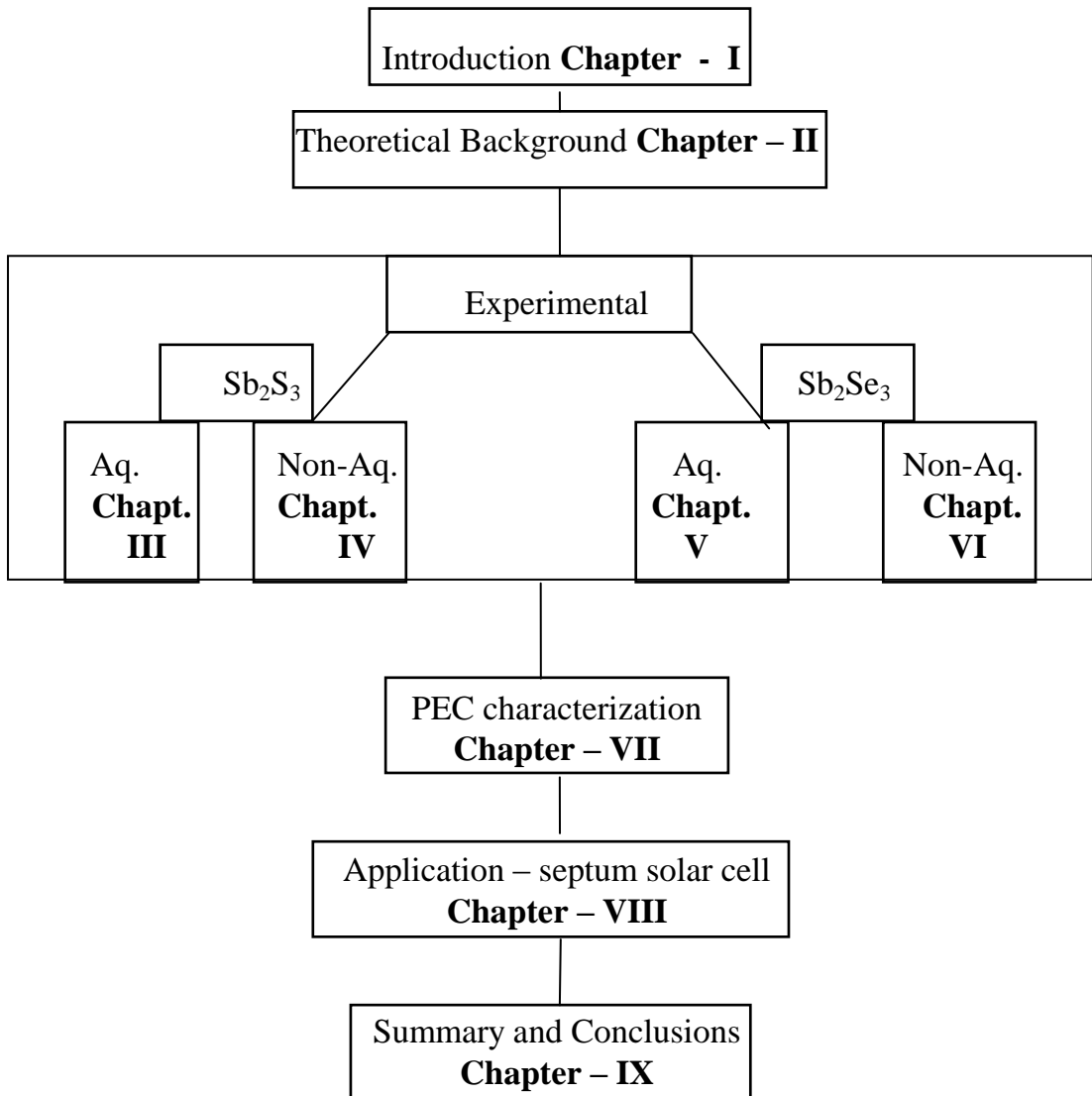
K. Y. Rajpure

Place : KOLHAPUR

Date :

STRUCTURE OF THE THESIS

The thesis is organized to use the ‘Spray Pyrolysis’ technique to deposit Sb_2S_3 and Sb_2Se_3 thin films from aqueous and non- aqueous medium. The prepared films are characterized by various techniques for their structural, optical, electrical and (photo) electrochemical properties. These films are used as a semiconductor septum electrode in PEC based storage cell. The thesis is structured in 9 phases, which are shown in the following flow chart:



List of Publications based on the Research Work :

a) *Papers published / accepted / submitted to the cited Journals and Proceedings*

1. **J. Materials Chemistry & Physics, Taiwan, 51(1997)252.**
K.Y.Rajpure, C.D.Lokhande and C.H.Bhosale
A comparative study of concentration effect of complexing agent on the properties of spray deposited Sb_2S_3 thin films and precipitated powders
2. **Thin Solid Films , 311(1997)114.**
K.Y. Rajpure , C.D. Lokhande and C.H. Bhosale
Substrate temperature dependent properties of sprayed Sb - Se thin films prepared from *non*-aqueous medium
3. **J. Materials Chemistry & Physics , 56(1998)177.**
K.Y. Rajpure , A.L. Dhebe, C.D. Lokhande and C.H. Bhosale
Effect of relative amounts of complexing agents on the properties of Sb_2S_3 precipitated powders
4. **physics status solidi (a), Vol. 172, No. 2 (1999) 415.**
K.Y. Rajpure, P.A. Anarse, C.D. Lokhande and C.H. Bhosale
Photoelectrochemical studies on electrodeposited Cd-Fe-Se thin films
5. **J. Materials Research Bulletin, Vol. 34 No. 1 (1999)**
K.Y. Rajpure, C.D. Lokhande and C.H. Bhosale
A comparative study of the properties of spray deposited Sb_2Se_3 thin films prepared from aqueous and non-aqueous media
6. **Materials Chemistry and Physics, 59 (1999) 237.**
V.V. Killedar, K.Y. Rajpure, P.S. Patil and C.H. Bhosale
Transient photoconductivity measurements of spray deposited Sb_2S_3 and Bi_2S_3 thin films from non-aqueous medium
7. **Bulletin of Materials Science (1999) (In Press)**
K.Y. Rajpure , V.L. Mathe and C.H.Bhosale
Photoelectrochemical investigation on spray deposited *n*- CdIn_2S_4 thin films
8. **Indian J. Pure and Applied Physics (1998) (Revised Submitted)**
K.Y. Rajpure , S.M. Bamane , C.D. Lokhande and C.H.Bhosale
Structural , optical and (Photo)electrochemical Properties of Electrodeposited Cd-Zn-Se Thin Films
9. **J. Physics and Chemistry of Solids, (1998) (Revised Submitted)**
Effect of composition on the structural, optical and electrical properties of sprayed Sb_2S_3 thin films prepared from *non*-aqueous medium
K.Y. Rajpure, C.D. Lokhande and C.H. Bhosale

10. **Materials Chemistry and Physics, (1999) (Revised Submitted)**
A.P. Torane, K.Y. Rajpure & C.H. Bhosale
Preparation and characterization of electrodeposited Sb_2Se_3 thin films
11. **Materials Chemistry and Physics, (1999) (In Press)**
K.Y. Rajpure and C.H. Bhosale
Effect of Se source on properties of spray deposited Sb_2Se_3 thin films
12. **Turkish Journal of Physics, (1998) (Submitted)**
K.Y. Rajpure, C.D. Lokhande and C.H. Bhosale
Optical properties of spray deposited Sb_2Se_3 thin films prepared from aqueous and non-aqueous media : A comparative study
13. **Thin Solid Films , (1998) (Submitted).**
K.Y. Rajpure , C.D. Lokhande & C.H. Bhosale
Preparation and characterisation of photoactive spray deposited Sb_2S_3 and Sb_2Se_3 thin films prepared from aqueous and *non*-aqueous media
14. **Turkish Journal of Physics (1999) (Submitted)**
K.Y. Rajpure , A.M. Patil, C.D. Lokhande & C.H. Bhosale
Substrate temperature dependent properties of spray deposited indium sulphide thin films
15. **Trans. SAEST, Karaikudi (1999) (Submitted)**
K.Y. Rajpure , V.L. Mathe and C.H. Bhosale
Properties of photoelectrochemical cell formed with sprayed CdIn_2S_4 thin films.
16. **Materials Chemistry and Physics, (1999) (Submitted)**
K.Y. Rajpure, M.N. Kusumade and C. H. Bhosale
Effect of Sb doping on properties of conductive spray deposited SnO_2 thin films
17. **Materials Chemistry and Physics, (1999) (Submitted)**
K.Y. Rajpure and C.H. Bhosale
(Photo)electrochemical investigations on spray deposited *n*- Sb_2S_3 thin film / polyiodide / C photoelectrochemical solar cells
18. **Materials Chemistry and Physics, (1999) (Submitted)**
K.Y. Rajpure and C.H. Bhosale
 Sb_2S_3 Semiconductor - Septum Rechargeable Storage Cell
19. **Materials Chemistry and Physics, (1999) (Submitted)**
K.Y. Rajpure and C.H. Bhosale
A study of substrate variation effects on the properties on *n*- Sb_2S_3 thin film/ polyiodide/ C photoelectrochemical solar cells
20. **Proceedings of NSEC-96, National Solar Energy Convention - 1996 , Jadavpur University ,Calcutta , Dec. 27- 29, 1996.**
K.Y. Rajpure , C.D. Lokhande and C.H. Bhosale
Properties of spray deposited Sb_2S_3 thin films
21. **Ninth International Workshop on Physics of Semiconductor Devices (IWPSD-97).**

SSPL, New Delhi (India). Published in : "Physics of Semiconductor Devices - Volume II", Editors : Vikram Kumar & S. K. Agarwal, Narosa Publishing House, New Delhi, (1998) pg. 1233.

K.Y.Rajpure and C.H.Bhosale

Solution concentration dependent properties of spray deposited Sb_2S_3 thin films

b) ***Papers presented / accepted at Conference / Seminars / Symposia***

- 1) " Preparation and characterization of monolithic silica Aerogels "
A. Venkateswara Rao , P.B .Wagh , D. Haranath and K.Y.Rajpure
National Conference on developments in Electronic Materials & Their Applications (NCDEMA) ; Shivaji University , Kolhapur (India) , march 6-8,1995.
- 2) " Sol - Gel processing and characterization of Silica gels and glasses "
A. Venkateswara Rao , D. Haranath , P.B.Wagh and K.Y.Rajpure
National Conference on Developments in Electronic Materials and Their Applications (NCDEMA); Shivaji University , Kolhapur (India) , March 6-8, 1995.
- 3) " Synthesis and physical properties of organic acid (Citric acid) catalyzed TEOS silica Aerogels "
P.B.Wagh , D. Haranath , A.Venkateswara Rao and K.Y.Rajpure
Three one day seminars on "New materials", Shivaji University, Kolhapur (India)March 5, 6 & 18 , 1996.
- 4) " Effect of concentration of complexing agent on the properties of spray deposited Sb_2S_3 thin films "
K.Y. Rajpure and C.H.Bhosale
Seventh National Convention / Conference of Electrochemists ", Shivaji University Kolhapur (India) , Nov. 18- 20, 1996.
- 5) " Effect of concentration of complexing agent on the properties of precipitated Sb_2S_3 powders"
K.Y. Rajpure and C.H.Bhosale
Seventh National Convention / Conference of Electrochemists ", Shivaji University Kolhapur (India) , Nov. 18- 20, 1996.
- 6) "Preparation & characterization of spray deposited CoS thin films"
K.Y. Rajpure, A. S. Sapkal and C.H.Bhosale
Seventh National Convention / Conference of Electrochemists ", Shivaji University Kolhapur (India) , Nov. 18- 20, 1996.

- 7) "Solution concentration dependent properties of spray deposited Sb-Se thin films from
non-aqueous medium"
K.Y.Rajpure and C.H.Bhosale
Symposium on current Status on Solar Energy Materials and Systems,
Anna University, Chennai (India), Feb. 24-25, 1997.
- 8) "Substrate temperature dependent properties of spray deposited Sb_2Se_3 thin films"
U. L. Shinde, K. Y. Rajpure and C. H. Bhosale
National Conference on Emerging Trends in Electrometallurgy and Eighth
National Convention of Electrochemists", Abstracts 1998, Jan. 28-30; 13(A).
- 9) "Preparation and Characterisation of $Sb_2(S_xSe_{1-x})_3$ pellets"
R. A. Vanjari, K. Y. Rajpure and C. H. Bhosale
National Conference on Emerging Trends in Electrometallurgy and Eighth
National Convention of Electrochemists", Abstracts 1998, Jan. 28-30;
19(A).
- 10) "(Photo)electrochemical Characterisation of Sprayed Bi_2S_3 thin films
prepared from
non-aqueous media"
V. V. Killedar, K. Y. Rajpure, C. D. Lokhande and C. H. Bhosale
Seminar cum Workshop on Materials and Characterisation, 13-17 July,
1998, CECRI, Karaikudi, T.N. (India).
- 12) "Preparation and Characterization of Photoactive Spray Deposited Sb_2S_3 and
 Sb_2Se_3 Thin Films Prepared from Aqueous and Non-aqueous Media"
K. Y. Rajpure, C. D. Lokhande and C. H. Bhosale
The Twelfth International Conference on "Photochemical Conversion
and Storage of Solar Energy" (IPS-12) held during 9 to 14 Aug. 1998 at
Hahn - Meitner Institut, Department of Physical Chemistry, Glienicke
Str. 100, 14109 Berlin, Germany.
- 13) "Properties of photoelectrochemical cells formed with sprayed $CdIn_2S_4$ thin
films" K.Y. Rajpure, V.L. Mathe, C.D. Lokhande and C. H. Bhosale
- 14) "Substrate temperature dependent properties of sprayed $CdIn_2S_4$ thin
films"
A.M. Patil, K.Y. Rajpure, C.D. Lokhande and C. H. Bhosale
- 15) "Effect of Sb doping on properties of spray deposited SnO_2 thin films"
K.Y. Rajpure, M.N. Kusumade, S.S. Kumbhar, C.D. Lokhande and C.
H. Bhosale
- Paper No. 13 to 15 are presented at the National Seminar on Recent
Trends in Solid State Sciences (NSRTSS-98) held at Sri Venkateswara
University, Tirupati (A.P.) during Nov., 23-24, 1998.
- 16) " Sb_2S_3 Semiconductor - Septum rechargeable storage cell"
K.Y. Rajpure, C.D. Lokhande and C.H. Bhosale,

International Conference on Energy Storage Techniques and Systems (ICOESTS), Energy Storage for meeting Power Crisis : A Futuristic Option, School of Energy and Environmental Studies, Devi Ahilya University, Indore, 1-4, Feb. 1999.

- 17) "Optical properties of CdIn_2S_4 thin films and their use in photoelectrochemical cells"
K.Y. Rajpure, V.L. Mathe, C.D. Lokhande and C.H. Bhosale
Regional Workshop on Characterization of Semiconductor nanostructure and their Application to Optoelectronic Devices University of Delhi, Dec., 1-4, 1998.
- 18) "Effect of Al doping on properties of spray deposited SnO_2 thin films"
K.Y. Rajpure, S.S. Kumbhar, M.N. Kusumade, C.D. Lokhande P.S. Patil
and C. H. Bhosale
- 19) "Structural and optical properties of electrodeposited In_2Te_3 thin films"
R.P. Pawar, K.Y. Rajpure and C. H. Bhosale
- 20) "Structural, optical and photoelectrochemical (PEC) properties of electrodeposited In–Se thin films"
A.D. Patil, K.Y. Rajpure and C. H. Bhosale
- 21) "Preparation and Characterization of Photoactive Spray Deposited Sb_2S_3 and Sb_2Se_3 Thin Films Prepared from Aqueous and Non-aqueous Media"
K. Y. Rajpure, C. D. Lokhande and C. H. Bhosale
- 22) "Photoelectrochemical investigation on spray deposited $n\text{-CdIn}_2\text{S}_4$ thin films"
K.Y. Rajpure, V.L. Mathe, C.D. Lokhande and C. H. Bhosale

Paper Nos. 18 to 22 are presented at the DAE- BRNS Symposium on Electro and Magnetoceramics held at Shivaji University, Kolhapur during Feb. 18- 20, 1999.

INDEX

Chap. No.	TITLE	Page Nos.
I	Introduction	1-18
II	Theoretical Background	19-51
III	Preparation and Characterisation of Sb_2S_3 Thin Films From aqueous Medium	52-74
IV	Preparation and Characterisation of Sb_2S_3 Thin Films From non- aqueous Medium	75-91
V	Preparation and Characterisation of Sb_2Se_3 Thin Films From non- aqueous Medium	92-110
VI	Preparation and Characterisation of Sb_2Se_3 Thin Films From non- aqueous Medium	111-135
VII	(Photo)Electrochemical Characterization of Antimony Chalcogenide Thin Films	136-172
VIII	Sb_2S_3 Based Semiconductor Septum Storage Cells	173-186
IX	Summary And Conclusions	187-206