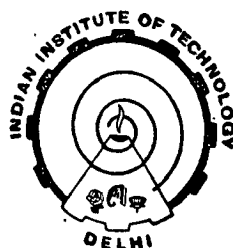


PREPARATION AND CHARACTERIZATION OF  
FLASH EVAPORATED LEAD-MERCURY CHALCOGENIDE  
SEMICONDUCTOR FILMS

by  
**MUKESH JAIN**

Thesis submitted to  
Indian Institute of Technology, Delhi  
for the award of degree of  
**DOCTOR OF PHILOSOPHY**



**Department of Physics**  
**INDIAN INSTITUTE OF TECHNOLOGY, DELHI**  
**FEBRUARY, 1985**

TO MY PARENTS

CERTIFICATE

This is to certify that the thesis entitled  
"Preparation and Characterisation of Flash Evaporated  
Lead Mercury Chalcogenide Semiconductor Films", being  
submitted by Mr. MUKESH JAIN to the Indian Institute of  
Technology, Delhi, for the award of the degree of Doctor  
of Philosophy in Physics is a record of bonafide research  
work carried out by him. Mr. Mukesh Jain has worked  
under my guidance and supervision for the submission  
of this thesis.

The thesis or any part there of has been submitted  
to any other university or institution for the award of  
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*Certified that the amendments proposed for the  
thesis have been incorporated in this copy.*

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22/11/85  
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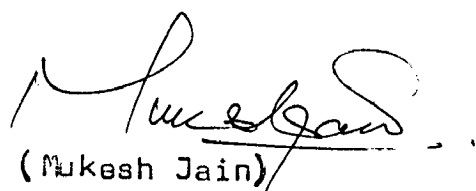
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(Mukesh Jain)

## ABSTRACT

Structural, optical and electrical properties of thin films of lead-mercury chalcogenide systems, flash evaporated on glass and freshly cleaved single crystal KBr substrates maintained at different temperatures, are reported in this thesis.

Results of investigations show that it is possible to grow single phase  $Pb_{1-x}Hg_xS$  ternary alloy films over a composition range  $0.07 \leq x \leq 0.93$ . The films grow by an atom-by-atom condensation process. Bonding orbitals of the adatoms appear to retain their character as in  $PbS$  ( $a = 5.936 \text{ \AA}$ ,  $F_{m3m}^{-O_h}$ )<sup>78-81</sup> and  $\alpha$ - $HgS$  ( $a = 4.15 \text{ \AA}$ ,  $c = 9.50 \text{ \AA}$ ,  $D_3^4$ )<sup>88-91</sup>, and hence the resulting ternary compounds behave as if they were apparent alloys of the two binary semiconductors. Available freedom of overlap and directional orientation of the interacting orbitals, which determine the lattice and band structures of the resulting alloys, depends on adatom mobilities which are controlled by the temperature of substrates during growth. It is observed that single phase f.c.c.  $Pb_{1-x}Hg_xS$  films can be grown over the composition range  $0.07 \leq x \leq 0.93$  on substrates maintained at  $100^\circ\text{C}$ . Epitaxy can be achieved in the lead rich ( $0.07 \leq x \leq 0.50$ ) films if the film were deposited on freshly cleaved KBr substrates maintained at this temperature. Films grown under the restricted adatom mobilities on substrates at  $50^\circ\text{C}$  and  $25^\circ\text{C}$  show that the lattice parameters of the lead rich films increase with decrease in substrate temperature, whereas, crystal structures of mercury rich films change to simple cubic in the  $T_g$  of  $50^\circ\text{C}$  and amorphous in  $T_g$  of  $25^\circ\text{C}$  films. The low symmetry structures can be modified to those with higher

symmetries by thermal and laser beam annealing of the films. Optical absorption studies indicate presence of a direct and an indirect optical gap in lead rich  $Pb_{1-x}Hg_xS$  films, whereas, the mercury rich films show a direct band gap only. The direct optical gap can be varied almost linearly between 1.43 eV and 2.17 eV by change in mercury concentration between 0.07 and 0.93 in polycrystalline f.c.c. films. The band gap is observed to decrease with increase in structural perfection of the lattices in the films. Electrical conductivity measurements suggest the predominance of impurity conduction upto 400 K beyond which the films show irreversible changes. The low (150 K) and high (300 K) temperature activation energies are observed to increase with increase in mercury concentration in the films. The low temperature activation energies appear to correspond to tunneling of charge carriers across the barriers, whereas, the high temperature activation energies correspond to the thermal excitation over inter-grain barriers. All the films show an increase in conductivity under illumination. Photoconductivity increases with increase in mercury concentration and decreases with increase in temperature of the films. Electrical and optical properties <sup>of</sup> amorphous mercury rich films indicate that the films behave like semiconductor even though the long range order is not present in these films.

Structural characteristics of the lead-mercury selenide films flash evaporated on substrates maintained between 25°C and 100°C show that single phase f.c.c.  $Pb_{1-x}Hg_xSe$  films can be grown over the composition range  $0.07 \leq x \leq 0.93$ . The films which grow by atom-by-atom condensation process behave as apparent alloy of  $PbSe$  ( $a = 6.147 \text{ \AA}$ ,  $F_m^3m - O_h^5$ ) and  $HgSe$  ( $a = 6.084 \text{ \AA}$ ,  $F_{43m}^o$ ). The lead rich ( $0.07 \leq x \leq 0.50$ ) films on single crystal KBr

substrates maintained between 70 and 100°C grow as epitaxial with  $\langle 100 \rangle$  zone axes orientations of their crystal grains.

Optical absorption and reflection measurements suggest the presence of a direct band gap in the films. The optical gap can be varied between 0.20 (0.15) eV and 0.09 (0.06) eV in the  $T_g$  of 25°C (100°C) films by changing the mercury concentration between 0.07 and 0.93. The electrical conductivity measurements indicate presence of predominant intrinsic conduction between  $\sim 400$  K and  $\sim 200$  K and impurity conduction upto  $\sim 200$  K. Conductivities of the films increase under IR illumination. The  $(\sigma_{ill} - \sigma_{dark}) / \sigma_{dark}$  ratio decreases with increase in mercury concentration and with increase in film temperature.

Structural investigations of the lead-mercury telluride films indicate that single phase f.c.c.  $Pb_{1-x}Hg_xTe$  films can be stabilised over a composition range  $0.07 \leq x \leq 0.93$  by appropriate choice of substrate temperatures. Lead rich ( $0.07 \leq x \leq 0.50$ ) films deposited on substrate between 25 to 100°C have f.c.c. lattices, however, the lattice parameters decrease slightly with increase in substrate temperature for the composition equivalent films. The lead rich films can be grown as epitaxial, with  $\langle 100 \rangle$  zone axes orientation of the crystal grains, on KBr single crystal substrates at 100°C. The mercury rich films, which grow as polycrystalline f.c.c. on substrates at 50°C and 100°C, deposit as amorphous mixtures of PbTe and HgTe on substrates at 25°C. Thermal, laser beam and electron beam annealings improve the structural symmetries of the as grown  $T_g$  of 25°C films. The optical gap is observed to vary between 0.27 (0.23) eV and 0.14(0.12) eV with change in mercury

concentration between 0.07 and 0.50 in the  $T_s$  of 25°C (100°C) films. The direct band gap in the  $T_s$  of 100°C mercury rich polycrystalline films can be varied between 0.13 eV and 0.09 eV by changing  $x$  between 0.60 and 0.93. The polycrystalline f.c.c.  $Pb_{1-x}Hg_xTe$  films behave as apparent mixtures of PbTe and HgTe. Activation energies calculated from  $\ln \sigma$  vs  $\frac{1}{T}$  curves indicate intrinsic conduction above  $\sim 325$  K and impurity conduction below this temperature. All films are observed to be photoconducting. The  $(\sigma_{ill} - \sigma_{dark})/\sigma_{dark}$  ratio is observed to decrease with increase in mercury concentration and the temperature of the films.

## CONTENTS

	Page
ACKNOWLEDGEMENTS	( i )
ABSTRACT	( ii )
CHAPTER I INTRODUCTION	1
CHAPTER II EXPERIMENTAL TECHNIQUES	15
2.1 Introduction	15
2.2 Deposition of Thin Films of Lead-Mercury Chalcogenides	15
2.2.1 Experimental Set-up	15
2.2.2 Preparation of the films	17
2.3 Electron Microscopy and Electron Diffraction Studies	18
2.4 Differential Thermal Analysis	20
2.5 Annealing of the Films	20
2.5.1 Thermal Annealing	20
2.5.2 Laser Beam Annealing	21
2.6 Auger Electron Spectroscopy	21
2.7 Optical Band Gap Determination of the Films	22
2.8 Dark - and Photo-conductivity	24
CHAPTER III STRUCTURAL, OPTICAL AND ELECTRICAL PROPERTIES OF FLASH EVAPORATED LEAD-MERCURY SULPHIDE FILMS	26
3.1 Introduction	26
3.2 Preparation of Samples	27
3.3 Structure of the Films	28
3.3.1 Transmission Electron Microscope Studies of As Grown Films: Experimental Results	28
3.3.2 Transmission Electron Microscope Studies of Annealed Films: Experimental Results	33

3.3.3. Differential Thermal Analysis	:	37
3.3.4 Analysis of the Experimental Results	:	38
3.4 Optical Properties	:	49
3.4.1 Experimental Results	:	49
3.4.2 Discussion	:	53
3.5 Electrical Properties	:	57
3.5.1 Experimental Results	:	57
3.5.2 Discussion	:	58
3.6 Conclusions	:	62
CHAPTER IV STRUCTURAL, OPTICAL AND ELECTRICAL PROPERTIES OF FLASH EVAPORATED LEAD-MERCURY SELENIDE FILMS	:	64
4.1 Introduction	:	64
4.2 Preparation of Thin Film Samples	:	65
4.3 Structure of the Films	:	66
4.3.1 Transmission Electron Microscope Studies of As Grown Films: Experimental Results	:	66
4.3.2 Transmission Electron Microscope Studies of Annealed Films: Experimental Results	:	69
4.3.3 Auger Electron Microscopy Results	:	70
4.3.4 Discussion of the Results:		71
4.4 Optical Properties	:	75
4.4.1 Experimental Results	:	75
4.4.2 Discussion	:	77
4.5 Electrical Properties	:	79
4.5.1 Experimental Results	:	79
4.5.2 Discussion	:	81
4.6 Conclusions	:	83

CHAPTER V	STRUCTURAL, OPTICAL AND ELECTRICAL PROPERTIES OF FLASH EVAPORATED LEAD-MERCURY TELLURIDE FILMS	:	85
	5.1 Introduction	:	85
	5.2 Preparation of Thin Film Samples	:	86
	5.3 Structure of the Films	:	87
	5.3.1 Transmission Electron Microscope Studies of As Grown Films: Experimental Results	:	87
	5.3.2 Transmission Electron Microscope Studies of Annealed Films: Experimental Results	:	90
	5.3.3 Auger Electron Microscopy Results	:	93
	5.3.4 Discussion of the Results:		94
	5.4 Optical Properties	:	98
	5.4.1 Experimental Results	:	98
	5.4.2 Discussion	:	100
	5.5 Electrical Properties	:	103
	5.5.1 Experimental Results	:	103
	5.5.2 Discussion	:	104
	5.6 Conclusions	:	107
CHAPTER VI	SUMMARY AND FUTURE SCOPE OF WORK	:	109
	REFERENCES	:	113
	LIST OF PUBLICATIONS	:	123