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

by
MUKESH JAIN

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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 any degree or diploma.

H. K. Sehgal

(Dr. H. K. Sehgal)
Department of Physics
Indian Institute of Technology, Delhi
New Delhi-110016

Certified that the ammendments proposed for the thesis have been incorporated in this copy.

H. K. Sehgal
22/11/85

(Dr. H. K. SEHGAL)

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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 ($a = 5.936$ Å, $F_m3_m-O_h^5$)[78-81] and α-HgS ($a = 4.15$ Å, $c = 9.50$ Å, D_3^4)[88-91], 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°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°C and 25°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_s of 50°C and amorphous in T_s of 25°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 of 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 Å, F_m3_m-O_h^5) and HgSe (a = 6.084 Å, $F_{\bar{4}3m}$). 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 <100> 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_s 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 ~400 K and ~200 K and impurity conduction upto ~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 stablised 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 <100> 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_s 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^oC (100^oC) films. The direct band gap in the T_s of 100^oC 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.

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