

STUDY OF DOPANTS IN LEAD CHALCOGENIDE

By
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Thesis submitted
in fulfilment of the
requirements of the degree of
DOCTOR OF PHILOSOPHY



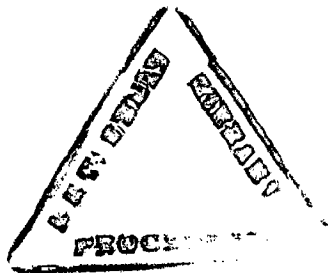
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C E R T I F I C A T E

This is to certify that the thesis entitled " **STUDY OF DOPANTS IN LEAD CHALCOGENIDES** " submitted by Mr. Rajesh Rampal has been prepared under my supervision in conformity with the rules and regulations of Indian Institute of Technology, Delhi. The research report and result presented in this thesis have not been submitted for any degree in any other university/Institution.

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ACKNOWLEDGEMENT

In the moment of completion of the research work. I wish to express my heartfelt sincere thanks and gratitude to my Supervisor Prof.O.P. Agnihotri for his valuable guidance and kind involvement throughout the course of the work. Without his overwhelming help, this work could not have been completed.

I am grateful to my Lab. colleagues particularly Dr.R.Thangraj and Mr. Stephan whom I have always troubled at odd hours. Probably without their help this work would have become extremely difficult. I am also grateful to Dr.S.P.Singh for fruitful and stimulating discussions. Dr.Raja Ram Polla, J.P.Mangalhari, Dr.A.Saxena have always been helpful to me. Nevertheless, the co-operation of Mr.G. Aren can not be forgotten. He was always ever ready to help me. I am also grateful to Miss Manju Gupta for her never refusing help in procuring books. Mr.Rathi and Miss Alpana contributed in their own way to make my working quite comfortable. I am also grateful to Mr.Rakesh, who typed my first rough draft of the thesis and supported me very well with his cheerful moods. Help rendered by Durgaprasad is also acknowledged.

Outside our laboratory, I am extremely grateful to Mr.Sunil Kumar, probably without his help things would have become very difficult. The affectionating help of Dr.A.N.Tiwari, Dr.Satyendra, Dr.A.Agarwal, Mr.Rastogi, Mukesh Bhatnagar was very gratifying. I am highly indebted to Dr.P.K.Gupta, Dr.K.Sharma from NPL and Mr.A.Shukla, Mr.V.D.Arora, Auntieji for their understanding during crisis.

I am also thankful to Mr.N.S.Gupta for his efficient drawing work and kudos to Mr.V.Saxena for his typing work.

Finally I have no proper words to express my deep sense of gratitude to my dear parents, my brother who has stood behind me like a rock at the time of my emotional crisis. I also gratefully acknowledge, MOT, my wife for bearing with my moods and temperaments.

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ABSTRACT

Lead tin telluride in an alloy system composed of two IV-VI compounds, PbTe and SnTe, referred to as pseudo-binary alloy. Both PbTe and SnTe have face centered cubic crystal structure. These compounds show complete solid solubility for any composition. The energy gap of these lead chalcogenides (Sulphur, Selenium, Tellurium) varies with the temperature, composition, and pressure. In these compounds varying the alloy fraction, X, the melting point and band gap of the system can be varied. The band gap of PbTe and SnTe are 0.3 eV and 0.2 eV at 300°K respectively. Because of the variable band gap nature these compounds can be tailored to have longer cut-off wavelength in mid and far infrared region. In the present work single crystals of PbTe and $Pb_{1-x}Sn_xTe$ with $x=0.17$, $x=0.20$, $x=0.25$, $x=0.45$, and $x=0.88$ were grown by modified double zone Bridgman technique. The maximum temperature was always kept at 50°C above the liquid^u temperature. However crystals with $x=0.0$, $x=0.17$, $x=0.20$ and $x=0.25$ were studied in particular for their morphological, optical and electrical properties. This is because of the significance of these compositions suitable for infrared detection. Surfaces of all the crystals were having mirror like reflection. Crystals were cut normal to the growth axis. The dislocation density of the best recrystallised PbTe and $Pb_{0.8}Sn_{0.2}Te$ crystals were in the range of $10^2 - 10^3 \text{ cm}^{-2}$. The compositional variation of the crystals from the first to freeze part to end of crystal was found to be reduced on

recrystallisation. Compositional analysis across the surface of the Crystal wafer, measured by infrared spectrophotometer, for low carrier concentration, samples showed larger band gap at the centre than at the periphery of the crystals. The flat response area of the crystal wafer was found to be increased by the recrystallisation process. The typical values of Hall mobility after recrystallisation improved whereas carrier concentration decreased. Typical values before and after are ^{as} follows.

- a) For PbTe as-grown $\mu_{H_a} = 1.7 \times 10^3 \text{ cm}^2/\text{V-sec}$ and $N_{\text{PbTe}} = 3.8 \times 10^{17} \text{ cm}^{-3}$
- b) For PbTe, after recrystallization $\mu_H = 2.5 \times 10^3 \text{ cm}^2/\text{V-sec}$ and $N_{\text{PbTe}} = 8.5 \times 10^{16} \text{ cm}^{-3}$

The mobility variation with temperature ^{ure} followed a power law of $T^{5/2}$.

Fermi level stabilization for four recrystallised PbSnTe crystals of $x=0.0, x=0.17, x=0.20$ and $x=0.25$ were studied as a function of Temperature from 20°K to 300°K . It was found that Fermi energy stabilisation was only a very weak function of composition and temperature. PbSnTe crystals with higher composition became degenerate at low temperatures. It is known that defects introduces acceptor and donor levels in the compounds. Their role in Fermi level stabilisation could not be ascertained adequately.

Results from flash evaporated films suggested that satisfactory stoichiometric composition could be obtained only by depositing films at high rates ($40\text{-}50 \text{ \AA sec}^{-1}$) and ^{also} at high substrate temperature (400°C) Films were _λ found to be deficient in 'Sn' content for $x=0.20$ composition. All films in as-deposited condition were 'p' type except PbTe films which were generally 'n' type. The carrier type could be changed

by using compensating source.

Very thin layers CdTe/PbTe multilayer structure having 25 periods ranging in thickness from 24 Å/113 Å to 50 Å/200 Å were deposited on PbTe buffered layer of 9600 Å thickness. The complete structure was deposited in very clean conditions on a (111), optically polished & cleaved BaF₂ crystal. The substrate temperature was varied between 350 to 400°C. The deposition was carried out by a computer controlled quartz thickness monitor and the oxygen background pressure was monitored by a Quadrupole mass spectrometer and kept below 10⁻⁹ mbar of pressure. Reflectance spectra in UV and visible region were recorded and n & k values were calculated by using "SOPRA Spectroscopic Ellipsometer". The results agree reasonably well with the reported literature results in considering thin layer structure. Optical absorption spectra was analysed by applying Kronig-Penney model and taking into the consideration of nonparabolicity and temperature dependent effective masses. The results were found to agree well with the experimental results for n=1 miniband transitions. The quality of the film was assessed by Transmission electron micrographs. All films were single crystalline and homogeneous. It was found that only Indium formed compounds with PbTe, whereas Cd as a dopant incorporation only increased the carrier concentration. Therefore the carrier reduction by the simultaneous addition of (Cd+In) may be attributed to chemical changes in the compound. The tendency of the Indium atoms is believed to segregate at the grain boundaries and voids. Thus helping in overall homogenisation

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of the samples.

Various dopants like Cd, In, Sn, Al, Cr and Mn were doped in these structures. Their profiles were analysed for percentage composition by using Auger electron spectroscopy and X-ray photoelectron spectroscopy.

The surface oxidation results are also reported for flash evaporated films. From these results it was observed that films deposited at 400°K were oxidised for Pb and Sn elements. However no oxidation of Te was noticed. The film deposited at 300°K showed no traces of oxidation within the detection limits of instrument.

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