CHEMICAL MODIFICATION OF SOME AMORPHOUS CHALCOGENIDE THIN FILMS

By

SUNIL KUMAR

CENTRE FOR MATERIALS SCIENCE AND TECHNOLOGY

Thesis submitted in fulfilment
of the requirements of
the degree of

DOCTOR OF PHILOSOPHY

to the

INDIAN INSTITUTE OF TECHNOLOGY, DELHI

JANUARY, 1988

TO MY PARENTS

CERTIFICATE

We are satisfied that the Thesis entitled "Chemical Modification of Some Amorphous Chalcogenide Thin Films" presented by Sunil Kumar is worthy of consideration for the award of the Degree of Doctor of Philosophy and is a record of the original bonafide research work carried out by him under our guidance and supervision, and that the results contained in it have not been submitted in part or full to any other university or institute for the award of any degree/diploma.

(Professor K.L.Chopra)
Department of Physics
(Presently: Director
I.I.T.,Kharagpur)

(Dr. Subhash C.Kashyap)
Assistant Professor
Centre for Materials
Science & Technology

Indian Institute of Technology,Delhi
New Delhi - 110 016, India.

ACKNOWLEDGEMENTS

It has been a privilege to be a member of Thin Film Laboratory. I take this opportunity to express my profound gratitude to Professor K.L.Chopra and Dr.Subhash C.Kashyap for their valuable guidance, deep involvement and positive criticism which have tremendously contributed towards the completion of the present work.

This work has immensely benefited from the help and cooperation extended by all the members of Thin Film Laboratory, both past and present. In particular, I wish to register my sincere thanks to Professor L.K.Malhotra and Dr. D.K.Pandya for the useful discussions related to my work. It has been a pleasure to be associated with Drs.Bodh Raj, A.N.Tiwari, Ajay Kumar, G.B.Reddy, Satyendra Kumar, P.K.Gupta, Vandna Agarwal and Mr. M.Bhatnagar in the course of various experiments and measurements. I am thankful to my colleagues R.S.Rastogi, D.Sunil, Sanjay Kaul, Balvinder and Kanwaljit for providing a pleasant company and extending their full cooperation whenever needed. The help rendered by the technical staff of our laboratory is also gratefully acknowledged. I am also thankful to Mr.Dinesh Bhardwaj for meticulous typing.

The research fellowship of the Centre for Materials Science and Technology, I.I.T.,Delhi is highly acknowledged.

Finally, I am deeply indebted to all my family members for their continuous encouragement throughout my research work.

Sunil Kumar

(SUNIL KUMAR)

ABSTRACT

The present work is centred round the chemical modification of amorphous thin films of $Ge_{20}Se_{80}$, As_2Se_3 and GeTe by incorporation of bismuth and oxygen. The preparation techniques for obtaining the films include thermal evaporation and activated reactive evaporation (ARE).

Both a-$Ge_{20}Se_{80}$ and a-As_2Se_3 are p-type semiconductors, each with a high value of optical absorption coefficient and a sharp absorption edge corresponding to an optical bandgap of about 2 eV. Thermally evaporated thin films of $Ge_{20}Se_{80-x}Bi_x$ (x=2,4,10) and $As_2Se_{3-x}Bi_x$ (x=0.1, 0.2, 0.5) have been systematically characterized for their compositional, electrical, optical and structural properties. The role of bismuth in these chalcogenide thin films has also been investigated. Furthermore, the feasibility of junction devices with these new materials has been established by making a Schottky barrier (between Bi metal and bismuth modified a-As_2Se_3) solar cell. Thin films of a-GeTe have been modified with oxygen impurity incorporated by using ARE.

The amorphous nature of the films is established by x-ray and electron diffraction studies. The concentration of different elements present in the films lies very close to that of the corresponding bulk alloys. Further, the Auger depth profile analysis revealed a uniform concentration of the modifier throughout the film thickness.

Incorporation of bismuth into a-$Ge_{20}Se_{80}$ and a-As_2Se_3 thin films has been observed to increase the electrical conductivity, σ, by several orders of magnitude. The enhancement of σ in case of a-GeTe upon modification by oxygen is small (only one order of magnitude). Bismuth modified films show n-type conduction (as confirmed by both the sign and the temperature dependence of the thermoelectric power) with Bi $\geq$ 4 at.% whereas Bi contents in excess of 8 at. % are necessary to induce n-type conduction in the corresponding bulk glasses. Oxygen modified a-GeTe films, however, remain p-type.

An increased tailing of the band edges and a shift of the absorption edge towards lower energy occur as a result of bismuth addition to a-$Ge_{20}Se_{80}$ and a-As_2Se_3 films. Oxygen incorporation into a-GeTe, on the other hand, widens the optical gap. The correlation of the electrical and optical data suggests the existence of localized states at the conduction band edge due to the incorporation of impurities. The decrease of E_σ (electrical activation energy) being much larger than the decrease of half the optical gap, E_g^{opt}, indicates the unpinning of Fermi level with a shift towards the conduction band edge. This is corroborated by the x-ray photoelectron spectroscopy (XPS) results according to which bismuth atoms in the amorphous chalcogenide network are positively charged owing to an electronic charge transfer from Bi to Se atom. This Bi^+ defects are responsible for the reduction of C_3^+ (three-fold coordinated chalcogen atom) defects in the material and hence unpin the Fermi level leading to conductivity conversion and large increase in the electrical conductivity.

Low temperature diffusion of bismuth into a-As_2Se_3 films has been exploited for the first time to fabricate and characterize an all-thin film Schottky barrier solar cell (Bi/As_2Se_3:Bi). The n-type semiconductor (As_2Se_3:Bi) is obtained by thermally diffusing a part of the Schottky barrier metal (Bi) into p-type a-As_2Se_3 thin film. The remaining metal film forms the Schottky barrier with As_2Se_3:Bi layer. Typical open-circuit voltage (V_{oc}) and short-circuit current density (J_{sc}) of the solar cell are 300 mV and 140 $\mu A/cm^2$, respectively. The temperature dependence of the diode ideality factor, n, and the reverse saturation current density, J_0, suggests the dominance of tunneling via recombination states as the current transport mechanism for the device.

In conclusion, thin films of a-$Ge_{20}Se_{80-x}Bi_x$ and a-$As_2Se_{3-x}Bi_x$ have been made to exhibit n-type conduction with a concentration of bismuth nearly 4 at.% or above. The role of bismuth in the conversion of conductivity has been investigated. Low-temperature diffusion of bismuth into a-As_2Se_3 films has been exploited for fabricating a thin film Schottky barrier solar cell. The feasibility of modifying a-GeTe with a gaseous impurity (oxygen) has also been established.

CONTENTS

		Page
ACKNOWLEDGEMENTS		
ABSTRACT		(i-iii)
CHAPTER 1	INTRODUCTION	1
	1.1 Atomic Structure	2
	1.2 Electronic Structure	6
	1.3 Defects in Amorphous Semiconductors	8
	1.4 Electrical Transport in Amorphous Semiconductors	15
	1.5 Chemical Modification of Chalcogenide Amorphous Semiconductors	17
	1.6 Aim of the Present Work	21
	1.7 Thesis Plan	22
CHAPTER 2	EXPERIMENTAL TECHNIQUES	24
	2.1 Preparation of Bulk Alloys and Thin Films	24
	2.2 Monitoring of Thickness and Deposition Rate of Thin Films	26
	2.3 Differential Thermal Analysis	27
	2.4 Structural Analysis	27
	2.5 Compositional and Chemical State Analyses	28
	2.6 Electrical Measurements	29
	2.7 Optical Measurements	32
	2.8 Characterization of Schottky Barrier Solar Cells	32

CHAPTER 3	STRUCTURE AND CHEMICAL COMPOSITION OF THE FILMS	34
	3.1 Results and Discussion	34
	3.1.1 Structure of the Films	34
	3.1.2 Chemical Composition of the Films	35
	3.2 Conclusions	37
CHAPTER 4	ELECTRICAL PROPERTIES	38
	4.1 Introduction	38
	4.2 Results and Discussion	39
	4.3 Conclusions	45
CHAPTER 5	OPTICAL PROPERTIES	47
	5.1 Introduction	47
	5.2 Results and Discussion	48
	5.2.1 Optical Properties	48
	5.2.2 IR Properties	52
	5.3 Conclusions	54
CHAPTER 6	X-RAY PHOTOELECTRON SPECTROSCOPIC STUDIES	55
	6.1 Introduction	55
	6.2 Results and Discussion	57
	6.2.1 Photoelectron Spectra of Bismuth Modified $Ge_{20}Se_{80}$ and As_2Se_3 Films	57
	6.2.2 Photoelectron Spectra of Oxygen Modified GeTe Films	59
	6.3 Conclusions	60

CHAPTER 7	SCHOTTKY BARRIER (Bi/As_2Se_3:Bi) SOLAR CELLS	61
	7.1 Introduction	61
	7.2 Fabrication Process	62
	7.3 Results and Discussion	63
	7.4 Conclusions	67
CHAPTER 8	CONCLUSIONS AND SCOPE OF FURTHER WORK	69
REFERENCES		72
LIST OF PUBLICATIONS		
BIO-DATA		