1. PREFACE

1.1. INTRODUCTION

Thin solid film is a promising field without which the importance of the microelectronics is seldom realized. The past two decades have seen considerable amount of development in microelectronics particularly arising out of the pressing demands in the fields of electronics and computer technology. These establishments have been the outcome of researches carried out in solid state materials and thin films of such materials, which are rendering an excellent service for the workers within this field by covering all aspects of film, science and technology. The field is now so wide that specialization within it has started to occur, and there is a need to subdivide, and study and report on these individual aspects.

Fundamental research has led to a vast improvement in our understanding of thin films and surfaces and this in turn has resulted in a greater ability to fabricate devices with predictable, controllable and reproducible properties. Active and passive components can be obtained in thin film form using suitable masks adopting different deposition techniques. Cleanliness and the nature of the substrate, the deposition conditions and the post-deposition heat treatment are the essential parameters in the fabrication of thin film components and devices.
1.2. LITERATURE SURVEY

It is well known that the semiconducting film materials have important physical and chemical characteristics and that these are often sharply increased in the case of compounds and/or alloys. Owing to a number of practical applications in all the fields, these film materials are subjected to different investigations by various researchers [1-10]. Also it is observed that there are significant differences in the properties of films of the same material coated under different deposition techniques [11].

1.2.1 GERMANIUM:

Among many elemental and alloy amorphous semiconductors, Ge films have been studied extensively. Different preparation techniques such as UHV thermal evaporation [12,13] e-beam evaporation [14], plasma-assisted chemical transport [15], ion beam sputtering [16], hydrogen plasma-assisted chemical transport [17] and glow-discharge decomposition [18-20] have been used to produce germanium thin films. The structural properties of germanium films have been extensively studied by a number of workers [21-28]. Almost all the reports indicate that the vacuum deposited Ge films possess amorphous structure.

Sloope and Tiller [29] observed that the defect density decreased with increase in substrate temperature for Ge films grown on CaF$_2$ substrates. They showed [30] that the electrical
properties are improved by an increase in substrate temperature and attributed this to the decrease in the defect density. Vasilev and Tikhonova [31] showed that the defect density decreases with increase in substrate temperature for Ge films grown on Ge substrates. Kurov et al. [32] have measured the Hall constant and mobility of Ge films by coating the Ge substrate with a Sn layer. Dubey [33] studied the electrical properties of vacuum evaporated epitaxial germanium films on germanium substrates and reported that Hall mobility values of the films approached that of bulk at higher temperatures. Chopra and Bahl extensively studied the structural, electrical and optical properties of germanium films prepared by thermal evaporation [34]. Also many workers reported the results on the electrical properties of Ge films [35-41]. Chopra has given a complete review of work carried out on optical behaviour of amorphous semiconductors including Ge, Se and their compounds [42]. The effects of the deposition rate and substrate temperature upon the structure of Ge films deposited on GaAs substrates were studied by Rybka et al. [43]. Gilbert et al. [44], studied the effect of electron bombardment on vapour deposited germanium films and reported the substantial crystal growth in films after electron bombardment. Structural modifications in amorphous Ge films due to laser annealing have been reported by Vitali and Crea [45] and Kameswara Rao et al. [46]. Barthwal and Chopra determined the thermoelectric power of vacuum evaporated amorphous germanium films [47].
1.2.2. SELENIUM

As it is well known, Se is a material having many uses including electrostatic image processing [48,49]. Amorphous Se layers are widely used as pattern bearers in xerography. Several studies have been made on the nature of amorphous Se layers. The process of crystallization, the relaxation of the layer structure and the influence of doping on the structure was examined by many workers [50-56].

Ozenbas studied the amorphous to crystalline transition of Se thin films deposited onto aluminium substrates [57]. As most of the studies pointed out, Se readily crystallizes into a spherulitic pattern in hexagonal form which is composed of helical chains oriented along the c-axis of the unit cell [58,59]. There exists a wide range of activation energies for the crystallization of a-Se films in the literature, which probably reflects impurity, deposition rate, thickness and substrate effects [60-64].

It is well established that the structure on physical feature of a-Se layer depends markedly on the thermal condition during deposition of the layer [65,66] as well as on nature of the substrates [67].

Electrical properties of a-Se films have been studied thoroughly by Lakatos and Abkowitz [68,69]. Navarrete et al. have determined the optical properties of amorphous selenium films.
prepared by vacuum evaporation. Classical damped oscillator model has been used by them to fit the transmittance spectra [70].

Optical, photo-absorption and energy band gap studies and the effect of annealing on these parameters were carried out by Misra [71] and Misra and Sharma [72].

Recently Peled et al. used laser photodeposition method to prepare selenium films and studied their physical properties [73]. The phase conjugation in amorphous selenium thin films deposited on glass substrates by vacuum evaporation has been reported by Haro-Poniatowski et al. [74].

1.2.3 Ge\textsubscript{x}Se\textsubscript{1-x}

Recently chalcogenide films have drawn great attention of scientists because of their basic and applied aspects in various solid state devices. A common feature of this material is the presence of localized states in the mobility gap due to inherent defects and the absence of long range order. Among the number of chalcogenide materials, Germanium Selenide gains importance because of its potential applications such as high resolution inorganic electron resist and as optical storage material [75-80]. Various techniques such as sputtering [81], thermal evaporation [82], spin coating [83] and magnetron sputtering [84] have been used to deposit this material in thin film form. More recently, a method of preparing it by plasma-enhanced chemical vapour deposition (PECVD) was developed, which makes the
deposition stage comply with industrial requirements and compatible with any process [85,86].

Molnar and Dove [87] analysed the structural properties of flash evaporated Ge-Se thin films and reported that these films possessed short range atomic order in consistent with a solid solution of Ge and Se. Ball and Chamberlain [88] prepared thin film specimen of Ge$_x$Se$_{1-x}$ in the range 0.0 < x < 0.5 and studied their infrared structural properties. The structure of evaporated GeSe$_2$ films and the influence of annealing at the glass transition temperature were studied by extended X-ray absorption fine structure [EXAFS] by Nemanich et al. [89]. More recently Sunil Kumar et al. [90], carried out the X-ray photoelectron spectroscopy studies of n-type bismuth-modified amorphous thin films of Ge$_{20}$Se$_{80}$. Optical properties of vacuum evaporated GeSe thin films were extensively studied by Butterfield [91], Toth et al. [92], Street et al. [93] and El.Shair and Fouad [94]. Electrical properties of Ge-Se films were the subject of interest in the works of Katti et al. [95], Nang et al. [96] and El.Shair et al. [97].

Bhanwar Singh et al. [98] Goel and Kumar [99], and Ajay Kumar et al. [100] have studied the photo-conduction effects in Ge-Se thin films and concluded that the contraction depends strongly on the angle of deposition and post deposition treatment of the films. Fazekas [101] and Fernandez Guasti et al. [102] have studied the laser induced phase transition in amorphous GeSe films.
1.3 SCOPE OF THE PRESENT WORK

Even though a number of reports are available as seen in the previous section on the preparation and study of some physical properties, such as structural, electrical and optical properties of vacuum evaporated Ge, Se and Ge-Se films, sufficient informations are not available on the dielectric, electrical, laser damage threshold and mechanical properties. Also, no report is available on the preparation of Ge, Se and germanium selenide films by hot wall deposition (HWD) technique which is one of the few methods available for the preparation of thin films with bulk like properties [103].

The purpose of the present work is to prepare thin films of Ge, Se and Ge$_x$Se$_{1-x}$ by both vacuum evaporation and hot wall deposition methods and to study some of their physical properties, viz., structural, dielectric, electrical conduction, breakdown, optical, mechanical and laser induced damages.

1.4 DETAILS OF THE PRESENT INVESTIGATION

Chapter II discusses the details of film preparation techniques (both vacuum evaporation and hot wall deposition) and film thickness measurement technique.

The third chapter deals with the structural, microstructural analysis of the Ge, Se and Ge$_x$Se$_{1-x}$ films and composition analysis of the Ge$_x$Se$_{1-x}$ film using ESCA, EDAX and RBS techniques.
The dielectric studies of these films are given in Chapter IV. The thickness dependence of dielectric constant, the effect of aging and annealing on the dielectric parameters, the dependence of capacitance and loss factor on frequency and temperature are examined. The temperature coefficient of capacitance and permittivity and linear expansion coefficient are dealt in this chapter.

The electrical conduction studies, both a.c. and d.c. conduction of these films have been given in Chapter V. Here the dependence of the a.c. conductivity on frequency and temperature and the dependence of d.c. conductivity on temperature and field are discussed in detail.

Chapter VI deals with the optical properties of these films. From the obtained transmittance data, the optical constants such as absorption coefficient ($\alpha$), absorption index ($k_f$), refractive index ($n_f$) and the optical band gap ($E_g$) are determined.

Chapter VII presents the electrical breakdown studies on these films. Dependence of onset breakdown field on thickness and temperature of the films are explained.

Chapter VIII discusses the laser threshold damage studies on both vacuum evaporated and hot wall deposited films.

Chapter IX deals with the in-situ stress measurements of vacuum evaporated Ge, Se and Ge$_x$Se$_{1-x}$ films.
Finally, the important conclusion drawn from the studies on vacuum evaporated and hot wall deposited Ge, Se, and Ge\textsubscript{x}Se\textsubscript{1-x} films are summarized and presented in chapter X.

Part of the results presented in this thesis have been published in the form of the following papers:
1. Thickness dependence of damage threshold on germanium thin films.
2. Structure and electrical properties of thermally evaporated germanium thin films
   Proc. 79\textsuperscript{th} Indian Science Congress (Boroda, 1992), Part III.
5. DC electrical conduction and breakdown studies on germanium thin films.
6. In-Situ stress measurements and Young's modulus of germanium thin films.
7. Dielectric and conduction studies on amorphous selenium thin films.

8. In-Situ stress measurements on amorphous germanium thin films.

9. Laser damage threshold studies on vacuum evaporated amorphous Ge$_x$Se$_{1-x}$ thin films.
National conference on Vacuum Science and Technology, New Delhi, October, 1993, CP 04.

10. Optical properties of vacuum evaporated Ge, Se and Ge$_x$Se$_{1-x}$ thin films.
National conference on Vacuum Science and Technology, New Delhi, October, 1993, CP 06.

11. Structure, dielectric, conduction and breakdown studies on amorphous Ge$_x$Se$_{1-x}$ thin films.

12. Laser damage threshold studies and microstructural analysis on amorphous germanium thin films.

13. Structural, electrical and optical properties of hot wall deposited Ge, Se and Ge$_x$Se$_{1-x}$ thin films.
14. Electrical and optical breakdown studies on Ge, Se and Ge$\textsubscript{x}$Se$\textsubscript{1-x}$ thin films.

15. Composition analysis and optical properties of hot wall deposited Ge, Se and Ge$\textsubscript{x}$Se$\textsubscript{1-x}$ thin films.
Accepted for presentation at the 5$^{th}$ AGM, Material Research Society of India, Hyderabad, Feb, 1994.

16. Structure, dielectric, conduction and breakdown studies of hot wall deposited Ge, Se and Ge$\textsubscript{x}$Se$\textsubscript{1-x}$ thin films.
Accepted for presentation at the 5$^{th}$ AGM, Material Research Society of India, Hyderabad, Feb, 1994.

*17. Phase transitions and critical phenomena growth and dielectric studies of Ba$_{1-x}$Ca$_x$TiO$_3$ single crystals.
[Not related to the present work].
REFERENCES

27. P. BOHAL, L. JASTRABIK, D. CHVOSTAVA AND V. ZELEZNY, Vacuum,
41 (1990) 1466.
31. V. D. VASIL'EV AND A. A. TIKHONOVA, Growth of Crystals,
2 (1957) 53.
74. E.H. PONIATOWSKI, M. FERNANDEZ-GUASTI AND S.C. LOPEZ, 
75. H. NAGAI, A. YOSHIKAWA, Y. TOYOSHIMA, O. OCHI AND Y. MIZUSHIMA, 
76. A. YOSHIKAWA, O. OCHI, H. NAGAI AND Y. MIZUSHIMA, ibid, 
29 (1976) 677.
78. K.L. TAI, R.G. VADMISKY, C.T. KEMMERER, J.S. WAGNER, V.E. LAMPERTI 
46 (1985) 481.
81. A. YOSHIKAWA, O. OCHI, H. NAGAI AND Y. MIZUSHIMA, Appl. Phys. lett., 
31 (1977) 161.
84. Y. UTSUGI, A. YOSHIKAWA AND T. KITAYAMA, Microelectron. Eng., 
5 (1990) 411.
86. B. CROS, M. DUBOURG, J.P. MARTINEZ AND J.L. BALLADORE, 


