CHAPTER I

PREFACE

1.1 Introduction

The progress in the science and technology of thin films has brought revolutionary changes in electronic industries and even today it continues to be recognised as one of the frontier areas. Electronics, optoelectronics, communication and space science are some of the major fields which have highly benefited from the influence of thin film technology. Practically there is no area in Science, where the impact of thin film technology has not been felt directly or indirectly.

The steady interest over the last two decades in thin films of chalcogenides reflect their technical importance as well as their complex behaviour. Switching properties discovered and developed, generated a great deal of interest in the transport phenomena of chalcogenides. The Ovonic memory switching has turned out to be important in bipolar memory technology in the development of random access memory (RAM) and the non alterable read only memory (ROM). Another area of the eventual application of memory switching is in ultra large memories including those for archival storage based on amorphous to polycrystalline phase transition.

In the past few years, thin films of chalcogenide semiconductors have attracted much attention in an expanding variety of applications, viz., electronic and optoelectronic devices. One of the characteristics of such semiconductors is a high density of localised states in the normal forbidden energy gap. The literature survey reveals that the chalcogenide semiconducting thin films of group VB and V1B elements have important physical and chemical characteristics and that these are often sharply improved in the case of compounds/alloys. Owing to a number of practical applications, the thin films of this group of elements (i.e. elemental or alloy) have been subjected to different investigations by various researchers.

1.2 Literature survey

Antimony triselenide (Sb_2Se_3), one of the candidates of group VB and VIB elements has received major attention in recent years because of its potential applications in contemporary opto-electronic solid state devices. Particularly Sb_2Se_3 thin films, owing to their good optical, photoconductive, photoelectric, electric and switching properties, have wide applications in switching, videodisc and optical recording. The switching and memory devices are based on reversible phase transformation between the crystalline and amorphous states of this material.

1.2.1 Properties of bulk Sb_2Se_3

Sb_2Se_3 and the members Sb_2S_3 and B_2S_3 of the same family are isostructural and have an Sb_2S_3 type orthorombic lattice. Donges [1] and Hofman [2] have shown that Sb_2Se_3 is isostructural with Sb_2S_3 type. The X-ray diffraction studies have been carried out on Sb_2Se_3 by Tideswell et al [3] with the help of Fourier series for accurate determination of its atomic parameters.

The crystalline Sb_2Se_3 is orthorhombic ($a = 1.162 \pm 0.001$, $b = 1.177 \pm 0.001$ and $c = 0.3962 \pm 0.0007$ nm) of space group D_{2h}^{16} type D_8^5 with 20 atoms i.e., 4 molecules per unit cell [2,3]. Fig. 1(a) shows the general view of the structure of the compound Sb_2Se_3. The structure of Sb_2Se_3 consists of zig zag chains of Sb-Se-Sb with strong bonds of Sb-Se. The separation of Sb-Se varies from 0.2566 to 0.2777 nm oriented along the c axis. Projection of the chain structure onto the (010) and on (001) planes are shown in Fig. 1(b). Pairs of these chains are fastened together along 2_1 screw axis to form larger chains through sets of Sb-Se bonds of length 0.2988 nm. These larger chains are in turn, bonded into sheets roughly perpendicular to the b-axis through the sets of Sb-Se bonds, which are 0.326 nm in length. Finally, the sheets are held together to make the crystalline solid through 2 sets of Sb-Se bonds which are 0.346 nm and 0.374 nm long respectively. A projection of the unit cell structure onto a (001) plane is shown in Fig. 1(c).

The atomic radial distribution studies carried out on Sb_2Se_3 using electron [4-8] and neutron [9] diffraction suggest that the intramolecular bonds in the crystalline phase remain unbroken in the liquid state. The general feature of the structure factor and the distribution function for liquid Sb_2Se_3 is similar to that of amorphous state.

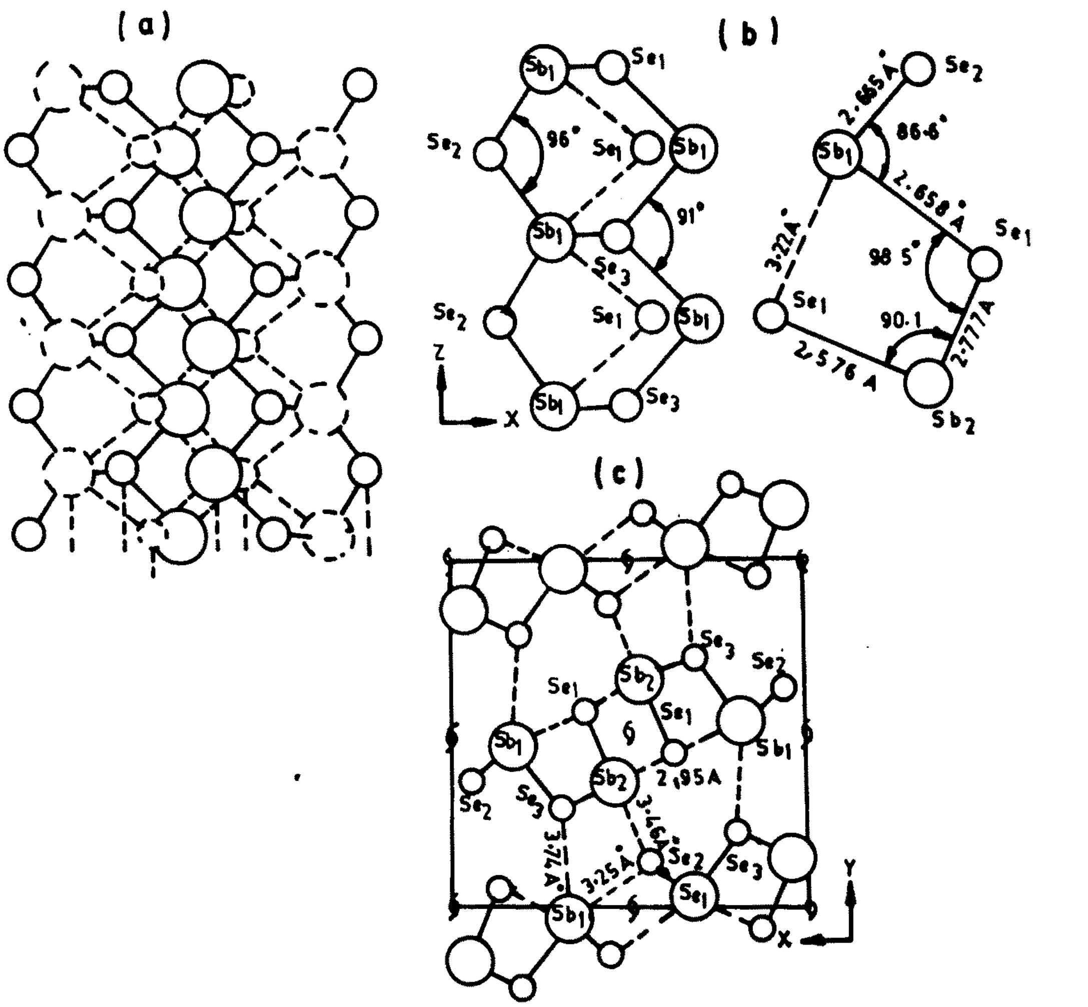

Fig 1·1 CRYSTAL STRUCTURE OF THE COMPOUND Sb_2Se_3 (a) GENERAL VIEW, (b) PROJECTION ONTO (010) AND (001) PLANES (c) PROJECTION OF A UNIT CELL ONTO A (001) PLANE

The transmittance and reflectance measurements of Kosek et al [10] on this parallel platelets of Sb_2Se_3 revealed the existence of indirect transition of bandwidth 1.12 eV. This value is in consistent with the reports of Gilbert et al [11], Skubenko and Leptu [12] and Shaffer et al [13]. The above value was appreciably higher than the value of 0.89 eV reported by Sobolev et al [14] and explained on the basis of the splitting of the valence band at the centre of the Brillouin zone into sub-bands [15]. Reflectivity study has been made by Shaffer et al on both single and amorphous bulk Sb_2Se_3 and confirmed the influence of the lack of long range order upon its electronic structure. It has been found as in other V-VI compound semiconductors [16] as well as in Te [17], the reflectance of amorphous material is significantly lower than that of the crystalline in the visible to near ultra-violet spectral range. This could result from a reduction of the average matrix elements for these transitions or from the reduction of the density of states in the energy range of interest. XPS measurements [18] on amorphous and crystalline Sb_2Se_3 indicate small differences in the magnitude of the valence band density of states in the energy range of interest. The transitions which dominate upto 8 eV in the reflectance spectra are associated with weak resonating p-bonds which were hypothicated by Mooser and Pearson [19] to occur in Sb_2Se_3 on the basis of the structural determination of Tideswell et al [3].

It follows from the results of Grigas and Valyukenas [20] on photoconductivity, photo emf and photoelectric properties of Sb_2Se_3 that an increase in the concentration of the impurity centers expands the impurity band which then merges with the valence band.

Kolomijec and Ljubin [21] reported the activation energy of 1.23 eV for Sb_2Se_3 from the electrical studies. Also Ignatev and Kor [22], Black et al [23] and Cullity et al [24] have determined the value of activation energy as $\simeq$ 1.0 eV, 1.4 eV and $\simeq$0.80 eV respectively. Based on electrical conductivity measurement, Kosek et al [10] have evaluated, the activation energy as 1.04 eV. The activation energies determined by earlier workers [21-24] were considerably different and it was attributed to the imperfect and non-stoichiometric compounds prepared. The dc conductivity studies of Mehra et al [25,26] on Sb-Se reveals clearly the nature of conduction mechanism to be of variable range of hopping type below 270 K and phonon assisted thermally activated type above 270 K.

Splat cooling Sb_2Se_3 [27] showed the switching characteristics of a memory switch which would be switched off only by cooling in liquid nitrogen in the presence of an electric field.

The study of Chakraborty et al [28] on thermoelectric power and Hall effect in Sb_2Se_3 revealed almost zero Hall coefficient and very low thermoelectric power. The failure to observe magnetoresistance indicates the very low mobility of charge carriers in Sb_2Se_3.

1.2.2. Properties of Sb_2Se_3 thin films

Semiconductor chalcogenide thin films have received major attention among scientists because of their applications in device fabrication [29]. A common feature of this material is the presence of localised states in the mobility gap due to inherent defects and the absence of long range order. Sb_2Se_3 thin films, one of the candidates of this group, owing to its good photoconducting [30,31], photoelectric [32] and switching [33] properties has wide applications in switching and memory, image converters and optical information recording [34-37]. These devices are based on reversible phase transformation between the crystalline and amorphous states of thin films.

The background history and results of the initial investigation on the vacuum evaporation and condensation of Sb_2Se_3 thin layers (5 - 15 μm) have been reported by Kolomiets et al [38]. Till then only thin layers of Sb_2Se_3 compounds were considered to be sensitive to infrared radiation [39].

The mass spectroscopy [40], Infrared spectroscopy, electron diffraction, nuclear gamma resonance [41] and Mossbauer [42] studies on these films indicate that both co-ordination number and the nearest neighbour distance was found to decrease in the transition from crystalline to amorphous phase. The degree of perfection of the texture of the films obtained on mica substrate was found to be less than for those on NaCl [43].

Very few workers have carried out investigation on optical absorption and photoconductivity of amorphous and polycrystalline films of Sb_2Se_3. In these studies analysis of absorption to obtain optical band gap and the nature of transitions to understand the band structure has been made. Shutov et al [44] from photoconductive measurements, reported the optical band gap of amorphous and crystalline Sb_2Se_3 films as 1.6 eV and 1.3 eV respectively. These results are appreciably higher than those of Wood et al[45] from photoconductive measurements and El-Shair et al [46] from transmission measurements which were explained based on the compositional deviation in the prepared samples. Reflectivity study made by Mueller et al [47] on amorphous $Sb_{1-x}Se_x$ films prepared from simultaneous evaporation confirmed the chemical alternations that occurred in the system. This may be probably due to conversion of Se-P electrons from the lone pair to bonding character. Wood et al [48] in another article reported the phonon assisted indirect transition in both amorphous and polycrystalline films. El-Shair et al [46] reported the existence of both direct and indirect transition in Sb_2Se_3 films. Recently, dependence of transport and optical properties of amorphous Sb_2Se_3 films on heat treatment have been reported by Zayed et al [49].

Alzewl et al [50,51] have studied electrical conductivity of powdered Sb_2Se_3. Electrical properties of chemically [52], sprayed [53] and vacuum [54] deposited films have also been reported. Fedoseeva [55] has investigated the dielectric properties of thermally evaporated amorphous films of Sb_2Se_3. Anomalies in electrical conductivity, dielectric and birefringence of Sb_2Se_3 single crystals have been reported by Grigas et al [56], while studying their temperature dependence (300-500 K). It was attributed to a diffuse phase transition in the semiconductor chain structure at 400 - 450 K. Parakh et al [57] have also reported anomalies in dielectric properties of polycrystalline Sb_2Se_3 films. Electrical resistivity measurements of El-Salam et al [58] in amorphous Sb_2Se_3 films revealed the dependence of activation energy with thickness and the free carrier concentration. Recently, switching phenomenon was observed by El-Salam et al [33] in amorphous Sb_2Se_3 films and was explained on the basis of electrothermal breakdown.

Development in optical recording technology in recent times brought a renewed interest in the phase change materials for use as optical recording media [59-63]. The work of Pirogov et al [64] on optical properties established the amorphous to polycrystalline phase transition of Sb_2Se_3 film due to illumination of light. The study of Barton et al [65] on amorphous films from simultaneous evaporation technique confirmed the switching between amorphous and polycrystalline states using the heat of a focussed laser. Kinetics of laser induced cyrstallization and oxidation of thin Sb, Se and Sb_2Se_3 was reported by Kolev and Wautlet [66]. Kolev and Laude [67] also reported the synthesis of a compound semiconducting thin layer of antimony chalcogenide. Possible applications of Sb_2Se_3 in optical WORM (write once and read many times) based on reflectivity were discussed. Pramanik and Bhattacharaya [68] developed a technique for the deposition of chalcogenide thin films by solution growth on polymer surface for device fabrication.

1.3 Scope of the present work

A thorough literature survey, as seen in the previous sections, reveals that although much work has been done on structural, optical and electrical properties of bulk Sb_2Se_3, reports on the physical properties of thermally deposited amorphous and polycrystalline films of Sb_2Se_3 are relatively less in number. Sufficient information is not available on the dc conduction, dielectric and optical recording characteristics of Sb_2Se_3 films. Also no systematic study has been made inorder to characterise the thin films of this material to use them for device applications.

Keeping this in mind, in the present investigation, a detailed study on the important physical properties such as structural, compositional, optical, electrical, thermoelectric, breakdown and optical recording characteristics have been carried out on thermally evaporated stiochiometric amorphous and polycrystalline Sb_2Se_3 films. An attempt has also been made to know its suitability as an optical storage medium.

1.4 Details of the present work

The investigation presented in this thesis comprises studies on vacuum deposited amorphous and polycrystalline films of Sb_2Se_3. The first chapter is of introductory nature and has been devoted to present the literature survey and to explain the importance of the present work, briefly.

The details of the experimental techniques employed in the present work such as the preparation of amorphous and polycrystalline films, fabrication of thin film structures and thickness measurement by multiple beam interferometry and quartz crystal thickness monitor have been dealt with in Chapter II.

The third chapter deals with the structural surface morphology and compositional analysis of both amorphous and polycrystalline films of Sb_2Se_3 using X-ray diffractogram (XRD), scanning electron microscope (SEM), energy dispersive analysis by X-rays (EDAX) and Rutherford back scattering (RBS) techniques.

Optical properties of vacuum deposited Sb_2Se_3 films have been presented in the fourth chapter. Optical parameters such as refractive index (n), extinction coefficient (k) and absorption coefficient (α) are obtained from the transmittance and reflectance spectra of various thicknesses. The optical transitions occurring at or near the band edges are discussed and the corresponding transition energies are estimated.

The dc conduction studies on these films have been given in

Chapter V. In this chapter, dc conductive measurements as a function of temperature and electric field on Sb_2Se_3 films are analysed to identify the conduction mechanism. The thermoelectric study has been carried out on Sb_2Se_3 films and the results are also discussed in this chapter.

The dielectric and ac conduction studies made on these films are given in the Chapter VI. The thickness dependence of dielectric constant of both amorphous and polycrystalline films, the effect of annealing on the dielectric parameters, the dependence of capacitance and loss factor on frequency and temperature are examined. The nature of ac conduction mechanism is also discussed in this chapter.

Chapter VII presents the electrical breakdown studies on these films. The thickness dependence of the breakdown field strength for these films have been studied and the breakdown mechanism has also been discussed.

Chapter VIII deals with the information about the optical recording characteristics of Sb_2Se_3 films. Using a beam probe technique in which CW-Ar^+ laser and the low power He-Ne laser are used as write and read beam respectively, the optical recording characteristics of Sb_2Se_3 films were studied based on amorphous to crystalline phase transformation. The effect of power, power density, time of laser irradiation, scanning speed and thickness of films on the percentage change in transmittance have been investigated and the results are analysed.

1.5 List of Publications

A part of the results presented in this thesis has been published in the form of the following papers.

1. Effect of Substrate Temperature and Rate of Deposition on Optical Properties of Sb_2Se_3 Thin Films, Proc. of the DAE, Solid State Physics Symposium, BARC, 36C (1993) 272
2. Structural Optical and Dielectric Properties of Vacuum Deposited Sb_2Se_3 Thin Films, National Symposium on Vacuum Science and Technology, National Physical Laboratory, New Delhi, 1993, cp-15
3. CW Laser Induced Structural and Optical Properties of As-deposited Sb_2Se_3 Films, International Conference on Vacuum Science and Technology and SRS Vacuum Systems, Centre for Advanced Technology, Indore, 1955 #029
4. Structural and Optical Properties of Sb_2Se_3 Thin Films, National Conference on Thin Film Processing and Applications, Sri Venkateswara University, Tirupathi,1995 p.70
5. Optical Recording Characteristics of Sb_2Se_3 Thin Films using CW-Ar^+ Laser, Thin Solid Films, (UK) (accepted for publication)
6. Anamalous Electric Conductivity in Sb_2Se_3 Thin Films, National Conference on Developments in Electronic Materials and Their Applications, Kolhapur,1995 p.53

7. CW-Ar^+ Laser Induced Structural and Optical Properties of Sb_2Se_3 Films, Materials Research Bulletin, (USA) (accepted for publication)

8. DC Conduction Studies on Sb_2Se_3 Thin Films
Physica Status Solidi, (accepted for publication)

9. Sb_2Se_3 Thin Films for Memory Device Applications
Technology-Journal of the PSG College of Technology and Polytechnic, March 1995 p.105

10. Structure Dielectric and AC Conduction Properties of Sb_2Se_3 Thin Films, Journal of Physics D: Applied Physics (communicated)

11 Optical Properties of Sb_2Se_3 Thin Films,
Physica Status Solidi (communicated)

REFERENCES

1. E.Donges, Z.anorg.Chem., 263 (1950) 289
2. W.Hofman, Z.Kristallogr, 86 (1933) 225
3. N.W.Tideswell, F.H.Kruse and J.D.McCullocor, Acta.Cryst., 10 (1957) 99
4. L.I.Tatarinova, Kristallogsafiya, 4 (1959) 678
5. Y.Sagara, O.Uemura, Y.Suzuki and T.Satow, Phys.Stat Sol.(a), 33 (1976) 691
6. B.I.Kazandzhan, Fiz.Tek.Poluprod, 2 (1968) 400
7. A.A.Andrev and Mamadaliev, J.Non-Cryst.Sol., 8-10 (1972) 287
8. O.Uemura and T.Satow, Phys.Stat.Sol.(b), 84 (1977) 353
9. Tsuneosatow, Osamu Uemura, Shigemoto Akaike, and Shigeru Tamaki, J.Non-Cryst.Solids, 29 (1978) 215
10. F.Kosek,J.Tulka and L.Stourac, Czech.J.Phys., B28 (1978) 325
11. L.R.Gilbert, B.VanPelt and C.Wood, J.Phys.Chem. Solids, 35 (1974) 1629
12. A.F.Skubenko and S.V.Leptu, Ukr.Fiz Zurnal, 9 (1964) 744
13. J.C.Shaffer, B.Van Pelt, C.Wood, J.Freeouf, K.Murase and J.W.Osmun, Phys. Stat.Sol.(b), 54 (1972) 511
14. V.V.Sobolev, S.D.Shutov and S.N.Shestatskh Moldavian, Acad.Sciences, USSR, 183 (1969)
15. A.Audzijonis, J.Batarunas, A.Karpur and S.Kudzmanskas, Lietuvos Fizikos Rinkiny, 5 (1965) 481
16. R.Zallen, R.E.Drews, R.L.Emerald and M.L.Slade, Phys.Rev.Lett., 26 (1971) 1564
17. J.Stoke, J.Non-Cryst.Solids, 4 (1970) 1

18. C.Wood, J.C.Shaffer and W.V.Proctor,
Phys.Rev.Lett., 29 (1962) 485

19. E.Mooser and W.B.Pearson J.Phys.Chem.Solids, 7 (1958) 65

20. B.P.Grigas and V.I.Valyukenas,
Sov.Phys.Semicond., 12 (1978) 1420

21. B.T.Kolomijec and V.M.Ljubin, Fiz.Tv.Tela., 1 (1959) 740

22. E.A.Ignatev and M.V.Kor,
Uczapiski Kisinevskogo gosuni, 24 (1956) 19

23. J.Black, E.M.Conwell, L.Seigle and C.W.Spencer,
J.Phys.Chem.Solids, 2 (1957) 240

24. D.P.Cullity, M.Telkes and J.T.Norton, J.Metals, 188(1950) 47

25. R.M.Mehra, Radhey Shyam and P.C.Mathur,
Phys.Rev.B, 19 (1979) 6525

26. R.M.Mehra, Radhey Shyam S.C.Agarwal and P.C.Mathur,
Phys.Lett., 75 A (1980) 409

27. D.Brasen, J.Non.Cryst.Solids, 15 (1974) 395

28. B.R.Chakraborty, B.Ray, R.Bhattecharya and A.K.Dutta,
J.Phys.Chem.Solids, A 1 (1980) 913

29. K.L.Chopra, in 'Thin film phenomena',
Mc Graw Hill NewYork, 1969

30. B.T.Kolomiets and A.Kh.Zeinaly, Fiz.Tverd.Tela,
1 (1959) 979

31. A.F.Skubnekov, UKR-FIZ Zurnal, 5 (1960) 787

32. M.V.Kot and S.D.Sutov,
Uc-Zapiski Kisinevskogo Gos University, 39 (1959) 45

33. F.Ab.El.Salam, M.A.Afify and EAb.D.El-Wahabb, Vacuum, 44 (1993) 17

34. M.Takenaga, N.Yamada, S.Ohara, K.Nizhiuchi, M.Nagashima, T.Kashihura, S.Nakamura and T.Yamashita, in 'Proc.Soc.Opt Inst.Eng'., Edited A.E. Bell and A.A.Jamberdino, 420 (1983) 173

35. Several Papers, in 'Proc.Soc.Photo-opt.Inst.Eng'., Edited by R.A.Sprague, 529 (1985)

36. Y.Nakane, SPIE Optical Mass Data Storage, 529 (1985) 76

37. K.Kolev, Proc.30th Inter.Tech Sci.Conf., Varna (1989)

38. B.T.Kolomiets, V.M.Lyubin and D.V.Tarkhin, Sov.Phys.Solid State, 1 (1959) 819

39. Braithwaite Proc.Phys.Soc., B64 (1951) 274

40. V.P.Zakharov, V.S.Gerasimenko, Yu.G.Pottavtsev and L.P.Kucherenko, Inorg.Mat., (USA), 10 (1975) 310

41. S.L.Ruby, L.R.Gilbert and C.Wood, Phys.Lett., 37A (1971) 453

42. L.I.Tartarinova, Kristallografiya, 4 (1959) 678

43. V.M.Kosevich and L.F.Zozulya, Sov.Phys.Crystallogr, 26 (1981) 364

44. D.Shutov, V.V.Sobolev, V.V.Popov and S.N.Shestatskii, Phys.Status Solid, 1 (1969) K23

45. C.Wood Z.Hurych and J.C.Shaffer, J.Non.Cryst.Solids, 8-10 (1972) 209

46. HT.El-Shair, AM.Ibrahim, EAbd.El-Wahabb, M.A.Afify and F.Abd.El-Salam, Vacuum, 42 (1991) 911

47. R.Mueller, J.C.Shaffer and C.Wood, Phys.Stat.Sol.(b), 59 (1973) K19

48. C.Wood, L.R.Gilbert, V.Van Pelt and B.Wolffing, Phys.Stat.Sol. (b), 68 (1975) K39

49. H.A.Zayed, A.M.Abo Elsoud, B.A.Mansour and A.M.Ibrahim, Ind. J.Pure and Appl.Phys., 32 (1994) 334

50. A.Alzewl, M.M.Sekkina and Z.M.Hanafi, Z.Phys.Chem., 94 (1975) 235

51. K.Alzewl, M.M.Sekkina and Z.M.Hanafi, Egypt.J.Phys., 12 (1981) 51

52. A.A.Agasiev and R.B.Muradov, UCh.Zap.Azerb.Uni.Ser.Fig.Mat.Nauk, 3 (1972) 82

53. R.N.Bhattacharya and P.Pramanik, J.Electrochem. Soc., 129 (1982) 1642

54. V.M.Kosevich and L.F.Zolulya, Kristallographiya, 26 (1981) 640

55. V.Fedoseeva Uch.Zap.Gork.Uni., 148 (1972) 83

56. J.Grigas, A.Kindurya, J.Meskauskas, A.Orlinkas and V.Orbonaicuis, Krist.Tech., 13 (1978) 638

57. N.C.Parakh and J.C.Garg, Jpn.J.Appl.Phys., 24 (1985) 889

58. F.Abd El-Salam M.A.Afify and E.Abd.El-Wahabb, Vacuum, 44 (1993) 111

59. P.C.Elements, Appl.Opt., 22 (1983) 3165

60. M.Terao, T.Nishida,Y.Miyauchi, S.Horigome,T.Kaku and N.Ohta, Proc.SPIE Opt.Mass Data Storage II, 105 (1986) 695

61. M.Chen, K.A.Rubin and R.W.Barton in Technical Digest of the Topical meeting on Optical Data Storage (optical Society of America, Washington 1985), p.187

62. M.Chen, K.A.Rubin, V.Marello, U.G.Gerver and V.B.Jipson, Appl.Phys.Lett., 46 (1985) 734

63. C.J.Vander Poel, D.J.Gravestejin, W.G.V.M.Rippens, H.T.L.P.Stockx and C.M.J.Van Vijen, J. Appl.Phys., 9 (1986) 1819

64. F.V.Pirogov, V.I.Gerbreder, K.K.Shvarts and Ya.A.Teteris, Sov.Phys.Solid State, 28 (1986) 1594

65. Roger Barton, Charles R Davis, Kurt Rubin and Grace Lim, Appl.Phys.Lett., 48 (1986) 1255

66. K.Kolev and M.Wautlet, Appl.Phys., A52 (1991) 192

67. K.Kolev and D.Laude, Appl.Surface Sci., 54 (1992) 358

68. P.Pramanik and R.N.Bhattacharya, J.Mat.Sci.Lett., 6 (1987) 1105