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INTRODUCTION

1.1 GENERAL

In recent years thin film technology has developed enormously due to the fact that one dimension of the film is negligible and that it is relatively easy to produce. The technology of thin film deals with films of thickness between tenths of a nanometer and several micrometers. The pivotal role of thin film technology in the development of such diverse and challenging frontiers as microelectronics, optical coatings and integrated optics, thin film supercoductivity and quantum engineering, micromagnetism, metallurgical coatings and amorphous materials, surface engineering and solar energy conversion devices is all too well known and is now recognized as a frontier area of microscience and microtechnology. New and even more exciting fields are also emerging. The driving forces behind the exploration of the new frontiers are : materials with micrometric and nanometric dimension and the industrial applications of microscience and microtechnology for the development of synthetic materials of tailored properties for VLSI/GSI, communiction, informtics and solar energy conversion, with decreasing size of active electronic devices, a higher packing density, higher speed performance and lower costs are obtained.[1]

Various deposition techniques can be employed to prepare semiconductors in the form of thin films. Thin film deposition techniques can broadly be classified as physical and chemical methods. Physical ones include (i) Evaporation (2) Sputtering, chemical ones include (i) Chemical vapour deposition (2) Spray pyrolysis (3) Electrodeposition (4) Anodization (5) Solution growth (6) Screen printing (7) Solution-gas interface etc.

Amongst above deposition techniques electrodeposition is found to be simple, attractive and less expensive technique. The growth rate can easily be controlled by varying current density and deposition time. The preparative parameters such as bath composition, pH, concentration of complexing agent, current density and deposition time can be optimized to get thin, uniform and adherent films.

1.2 SURVEY OF LITERATURE ON

1.2.1 Bi_2S_3 Thin Films

Bismuth trisulphide (Bi_2S_3) occuring naturally in grey crystalline form is referred to as 'Bismuth glance' or 'Bismuthinite'. Both natural and artificial crystalline forms belong to orthorhombic crystal structure. Bismuthinite exists as a long prismatic and vertically striated steel-gray to tin-White crystals which are generally joined into columner aggregates and closely resemble stibnite (Sb_2S_3) in appearance. It is isomorphous with stibnite and arsenic trisulphide (As_2S_3). Miller et al[2] and Peter[3] have reported on

photoelectrochemical (PEC) behaviour of anodically deposited Bi_2S_3 films. Chemical bath deposition method has been reported by Pramanik and Bhattacharya[4] from aqueous alkaline bath using triethanolamine (TEA) as a complexing agent and thiourea (TU) as a S^{2-} ion source. The films were amorphous in nature showing random distribution of small crystallites. Krishnamoorthy and Shivkumar[5] deposited Bi_2S_3 films using cleaved cleared surfaces of NaCl ,KCl, KBr and KI etc. as substrates by Hot wall chemical deposition technqiue. The films were found to be amorphous and polycrystalline depending upon growth temperature. Biswas et al[6] by using TEA and thioacetamide as the complexing agent and the sulphide ion source respectively prepared Bi_2S_3 thin films with a band gap 1.7 eV. Lokhande et al[7,8] deposited Bi_2S_3 thin films from an acidic as well as alkaline bath using sodium thiosulphate ($Na_2S_2O_3$) as a sulphide ion source. The optical band gap of the films was found to be 1.54 eV and the resistivity was between 10^5 - 10^7 ohm-cm. Bi_2S_3 films were prepared using 'Electrodeposition technique' by Lokhande and Bhosale.[9] However, a detailed study of the preparative parameters has not been reported. Chemical deposition of semiconducting Bi_2S_3 thin films from an acidic bath has been carried out by Desai and Lokhande.[10]

1.2.2 Sb_2S_3 Thin Films

Antimony trisulphide (Sb_2S_3) has both amorphous and crystalline forms. Grey mineral sulphide is called as 'Antimony glance' or 'Stibnite'. Orange and red form is amorphous in nature. Artificial crystals appear as greyish black needles having orthorhombic structure. Thin films of sulphides of antimony and bismuth formed by evaporation in vacuo at different substrate temperatures have been examined in electron diffraction studies by Badchhape and Goswami[11]. Electrical contacts of metals on 'vacuum evaporated' photosensitive Sb_2S_3 thin films have been studied by Mitchell and Denure[12]. The studies reveal that Ni,Au and pt makes blocking contacts whereas contacts of In,Ga,Al and Bi are ohmic. Cu,Ag and Pd contacts show poor stability and have very low breakdown voltage, they are not considered to be suitable contact materials for Sb_2S_3. 'Vacuum evaporation' technique has been employed to prepare Sb_2S_3 thin films by Ghosh and Varma[13,14] As deposited films were amorphous in nature. The absorption coefficient (α) is of the order of 10^7 m^{-1} and indirect band gap Eg is 1.7 eV. George and Radhakrishnan[15] obtained the Sb_2S_3 films by vacuum co-evaporation of antimony and sulphur onto glass substrates. The films exhibited p type conductivity and activation energy is found to be 0.75 eV. Nayak et al[16] formed Sb_2S_3 films by 'Dip and Dry' technique. Pawar et al[17,18] prepared Bi_2S_3,

Sb_2S_3 , As_2S_3 and $Sb_{2-x}Bi_xS$ films by ' solution-gas interface' technique. Solution growth technique has been used by Lokhande [19] to prepare Sb_2S_3 and As_2S_3 thin films. Savadogo and Mandal [20] reported on chemically deposited Sb_2S_3 films. By using spray pyrolysis technique Bhosale et al [21] prepared Sb_2S_3 films and found the indirect band gap energy 'Eg' to be 1.55 eV. Deshmukh et al [22] prepared Sb_2S_3 films by chemical bath deposition method and studied their photoelectrochemical (PEC) properties.

1.2.3 As_2S_3 Thin Films

In conection with histories of arsenic and realgar (As_4S_4), Greek and Roman writers used names arrhenicum and auripigmentum (arum-gold; pigmentum-paint) for golden-yellow arsenic trisulphide (As_2S_3). This, so called orpiment occurs in several shades of lemon-yellow small crystals or in foliated and fibrous masses. It has monoclinic crystal structure. There are two forms of orpiment, yellow α-As_2S_3 and red β-As_2S_3. Yamamoto et al [23] heated (in vacuum) high purity As and S in quartz ampoules to 973^{o}K for 24 hour to make up stoichiometric As_2S_3 films.

Salik and Nadiv [24] have carried out structural studies of photodissolution of Ag in the amorphous films, which were obtained by 'vacuum deposition'. They observed that for crystalline As_2S_3 films even after prolonged illumination no photodissolution occurs. By using solution gas interface

technique Pawar and Bhosale[25] obtained polycrystalline As_2S_3 thin films. Hajto et al[26] reported on spin coated As_2S_3 films. By 'Vacuum evaporation' technique Lukes et al[27] obtained the As_2S_3 films onto unheated glass substrates and have determined refractive index from ellipsometric data. Preparation and physico-chemical characterisation of Bi_2S_3, Sb_2S_3 and As_2S_3 thin films was reported by Desai[28]. Stoichiometric As_2S_3 films were obtained with ethylenediamine tetraacetic acid (EDTA) complexed bath using thioacetamide (TAM) as a S^{2-} ion source. By using 'chemical deposition' technique, the deposition time was 9 hour and absorption coefficient (α) is of the order of 10^7 m^{-1}.

1.3 PURPOSE OF DISSERTATION

The survey of literature shows that though some work has been carried out on chalcogenide thin films of Bi, Sb and As, in view of their wide applications, further investigations are required to make full use of their active properties. Hence in the present investigation it is planned to deposit Bi_2S_3, Sb_2S_3 and As_2S_3 thin films at room temperature using sodium thiosulphate ($Na_2S_2O_3 5H_2O$) as a sulphide ion source by the method of 'Electrodeposition.' The effect of addition of complexing agent on the properties of the film will be studied.

Electrodeposition of films will be carried out onto copper, stainless steel, brass, titanium and fluorine doped tin oxide (FTO) coated glass from acidic bath using sodium thiosulphate as a S^{2-} ion source. The bath parameters to be optimized are bath composition, pH, concentration of complexing agent, deposition time and current density. The film characterisation will be carried out using X-ray diffraction (XRD), scanning electron microscopy (SEM), optical absorption and photoelectrochemical (PEC) studies. From the XRD characterisation crystallinity of the films deposited from uncomplexed and complexed bath with annealing effect will be studied. Information regarding microstructure of films will be obtained from SEM micrographs at different magnifications. Optical absorption studies employing UV-VIS-NIR spectrophotometer will be undertaken in order to determine nature of the transitions involved and optical band gap energy estimation. The PEC cells will be formed by employing Bi_2S_3, Sb_2S_3 and As_2S_3 films as photoelectrodes. The PEC characterisation of the films will be done using different electrolytes. The cell properties such as current-voltage and capacitance-voltage will be studied.

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