Room Temperature Synthesis of Nanoporous Network of Copper Doped $MoBi_2Se_5$ Mixed Metal Chalcogenide Thin Films

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Abstract. Nanoporous Cu (I) doped $MoBi_2Se_5$ mixed metal chalcogenide (MMC) thin films were successfully deposited on glass substrate at room temperature by using arrested precipitation technique (APT), in which the release of metal ions were controlled by using suitable complexing agent. As deposited thin films were annealed at 150 ºC for two hours and examined for their structural, surface morphological, optical and compositional properties by means of X- ray diffraction (XRD), scanning electron microscopy (SEM), UV-Vis spectrophotometry and energy dispersive X-ray spectroscopy (EDS) techniques, respectively. It has been found that Cu (I) doped $MoBi_2Se_5$ MMC thin films possesses rhombohedral structure while nanoporous surface morphology with pore size 91 nm was observed in SEM images. The optical absorption study showed direct and allowed transition 1.40 eV band gap energy. EDS data showed close agreement with theoretically expected stoichiometric composition of Mo, Bi, Cu and Se elements. Effect of annealing on crystallinity and band edge shift of Cu (I) doped $MoBi_2Se_5$ MMC thin films were studied. These studies reveals that Cu (I) doped $MoBi_2Se_5$ is a best suited material for photoelectrode in PEC cell to get high conversion efficiency.

Keywords: MMC, APT, Thin films, Chalcogenides, SEM, EDAX.

1. INTRODUCTION

Recently, the synthesis and characterization of metal chalcogenide thin films have attracted great attention due to their luminous applications such as solar cells, sensors and laser materials [1]. Various methods have been reported to prepare chalcogenide thin films. In present investigation APT was employed to deposit Cu (I) doped $MoBi_2Se_5$ MMC thin films. APT has number of advantages such as, simplicity, it does not require any sophisticate instrument, no material wastage and easy coating of large surface area. APT is based on the controlled release of metal ions and chalcogenide ions in an aqueous alkaline bath into which substrate were immersed.

In this paper we report for the first time the synthesis of Cu (I) doped MMC thin films from aqueous solution using Mo-TEA, Bi-TEA, Cu-TEA complexes as source of Mo^{4+}, Bi^{3+} and Cu^{1+} and sodium selenosulphite (Na_2SeSO_3) as source of Se^{2-} ions at room temperature.

2. Experimental:

The reaction bath consists of appropriate volume of Mo-TEA, Bi-TEA, Cu-TEA complex. Aqueous ammonia solution was used to adjust p^H of the reaction mixture at 9. An appropriate volume of Na_2SeSO_3 solution was added to alkaline solution with constant stirring. The total volume of the reaction mixture made to 40 ml by adding double distilled water. Depositions were carried out at room temperature by dipping glass substrate vertically in to reaction mixture for different time interval. The film thickness of as deposited and annealed samples was measured by Surface Profiler (AMBIOS XP-1). UV-Vis Spectrophotometer (Shimadzu UV-1800) was used to determine absorption spectra of thin films in the wavelength range 300-1100 nm. The structural properties of thin films were investigated by X-ray Diffractometer (XRD) (Brucker AXS Model D8 Advance) using Cu kα (λ=1.5418A°) radiation. The Scanning Electron Microscopic (SEM) analysis and Energy Dispersive X-ray Analysis (EDAX) were performed on a scanning microscope (JEOL-JSM-6360A Analytical Scanning Electron Microscope).

3. Results and Discussions:

3.1. Growth mechanism:

The Na_2SeSO_3 solution added to the reaction mixture containing Mo-TEA, Bi-TEA and Cu-TEA complex solutions play dual role as a source of Se^{2-} ions as well as a reducing agent due to presence of excess Na_2SO_3 [2]. At alkaline pH = 9, Na_2SeSO_3 hydrolyses into Na_2SO_4, follows base catalyzed reaction and release Se^{2-} ions into the solution. When the ionic product (K_p) exceeds the solubility product (K_{sp}) the deposition of Cu (I) doped MMC thin films takes place by multinucleation process followed by ion-by-ion condensation of Mo^{4+}, Bi^{3+}, Cu^{1+} and Se^{2-} ions onto the substrate surface.

3.2. Optical analysis:

The plots of $(\alpha h\nu)^2$ vs. hν for as deposited and annealed Cu (I) doped $MoBi_2Se_5$ MMC thin films are shown in figure (1). The linear dependence of $(\alpha h\nu)^2$ vs. hν was obtained for n = 2 and this is in good agreement with the fact that Cu (I) doped $MoBi_2Se_5$

MMC thin films is a direct allowed transition type of semiconductor. The optical absorption coefficient was found to be greater than 10^6 m^{-1} supporting the allowed direct band transition of the material. The optical band gap energy of as deposited thin film was found to be 1.40 eV and that of for annealed sample was 1.33 eV. The decrease in band gap energy after annealing is in consistent in fact that the crystallinity of crystalline thin films improves on annealing [3].

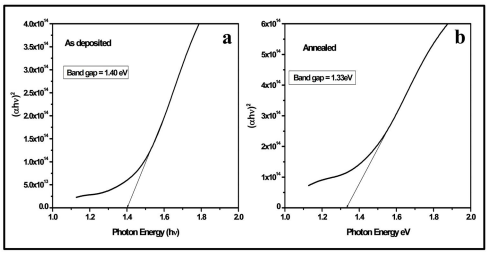

FIGURE 1. Plots of $(\alpha h\nu)^2$ versus hν plots.

3.3. XRD analysis:

Fig. 2 Shows typical XRD patterns of the as deposited and annealed Cu (I) doped $MoBi_2Se_5$ thin films with well defined peaks suggesting that the films were nanocrystalline in nature. XRD analysis shows that there is no characteristic peak corresponding to the impurity phase i.e. for Cu_2Se [4]. The individual crystalline size (D) has been determined as 19 nm for as deposited films and for the annealed films 28 nm using Scherrers formula.

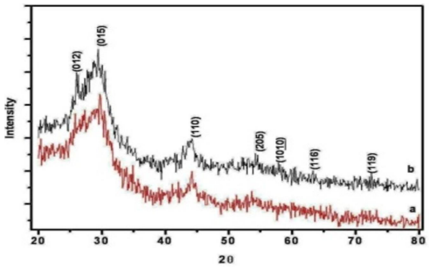

FIGURE 2: X-ray diffractograms of (a) as deposited, (b) annealed Cu (I) doped $MoBi_2Se_5$ thin films.

3.4. SEM analysis:

Figure 3 consist of SEM images Cu (I) doped $MoBi_2Se_5$ thin films which shows densely packed nanoporous network like morphology.

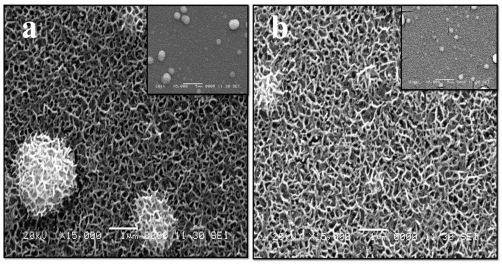

FIGURE 3: SEM mircograph of (a) as deposited and (b) annealed Cu (I) doped $MoBi_2Se_5$ thin film.

Twofold structure with an inner compact and outer porous layer was observed. This is due to change in growth from inner compact to outer porous layer with increasing deposition time [5]. The pore size 91 nm of as deposited samples decreases up to 84 nm after annealing. The reason behind the decrease in pore size may be due to the loss of trapped water that is water of crystallization after heat treatment which causes shrinking of pores.

3.5. EDS analysis:

The EDS spectrum (Fig. 4) of as deposited thin films shows successful doping of Cu (I) in to $MoBi_2Se_5$ thin films. Table (see inset of fig. 4) shows the elemental composition of Cu (I) doped $MoBi_2Se_5$ thin films in terms of atomic %. The increased atomic % of Bi than theoretically expected values is due to the more metallic character of Bi and its reactivity towards Se^{2-} is higher. Moreover bismuth forms antisite defects which is responsible for slightly non-stoichiometry of thin films.

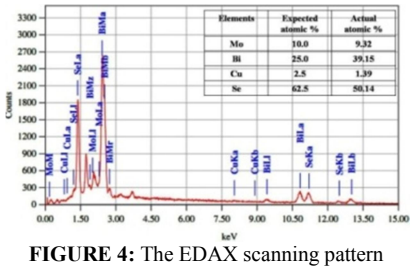

FIGURE 4: The EDAX scanning pattern

4. Conclusion:

Nanocrystalline Cu (I) doped $MoBi_2Se_5$ thin films were successfuly deposited by an inexpensive and simple APT at room temperature. A decrease in band gap was observed upon annealing. XRD study shows that films are nanocrystalline in nature with rhombohedral structure having crystallite size 20 nm. The crystallite size increased up to 28 nm after annealing. SEM images showed that the films consists of nanoporous network like morphology with pore size 91 nm which decreases up to 84 nm after annealing.

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