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Surfactant assisted synthesis of nanocrystalline n-Bi_2Se_3 thin films at room temperature via arrested precipitation technique

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In the present investigation, we have successfully synthesized nanocrystalline bismuth selenide (Bi_2Se_3) thin films using an arrested precipitation technique at room temperature. The optostructural, morphological, compositional and photoeletrochemical properties were studied for Bi_2Se_3 thin films prepared via surfactant-assisted synthesis. The optical study reveals the presence of direct allowed transition with band gap energy ranging from 1.40–1.80 eV. The X-ray diffraction (XRD) pattern confirms rhombohedral crystal structure. Scanning electron microscopy study shows the morphological transition from an interconnected mesh to nanosphere-like morphology and finally, lamellar sphere. Atomic force microscopy (AFM) study carried out to determine surface roughness and surface topography of thin films. Energy dispersive spectroscopy (EDS) analysis reveals the presence and ratio of elemental bismuth and selenium. Finally, the photoelectrochemical (PEC) performance of all the as-synthesized thin films were carried out using iodide-polyiodide redox couple.

Keywords: Bi_2Se_3, APT, surfactant.

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1. Introduction

Currently, there is significant research interest in the development of semiconducting materials for solar cell applications. Bi_2Se_3 is V-VI group binary chalcogenide which has been a material of interest for many years [1, 2]. The novel optostructural and morphological properties of Bi_2Se_3 are useful in numerous fields, such as thermoelectric devices, photosensitive devices, photovoltaic cells, Hall Effect magnetometer, refrigeration, high frequency power sensors, topographic insulator, etc [3–7].

Several methods have been developed to obtain nanostructured Bi_2Se_3 such as SILAR, MOCVD, CBD, Sputtering, Microwave assisted synthesis, etc. Among all these metods, APT is a simple, attractive and cost effective method. Hence, we have selected an APT method for deposition of Bi_2Se_3 thin films. There are very few reports available on the PEC performance of Bi_2Se_3 thin films. Hence, in the present article, we are reporting on the PEC performance for Bi_2Se_3 thin films prepared by a surfactant-assisted APT protocol.

2. Experimental

Nanocrystalline Bi_2Se_3 thin films have been synthesized via an arrested precipitation technique (APT) at room temperature. 0.05 M bismuth triethanolamine complex (Bi-TEA) and 0.25 M sodium selenosulphite (Na_2SeSO_3) were used as precursor solution for Bi and Se respectively. TEA was used as a complexing agent. In a typical synthesis, both precursor solutions were added in a 2:3 ratio. The pH was adjusted to 10. The pre-cleaned glass substrate was placed vertically in the reaction bath. The total volume of reaction bath was made 40 mL by addition of double distilled water (D/W). The reaction bath is maintained at room temperature without disturbing for 8 hrs. When the terminal growth stops, thin films were taken out and washed 2–3 times with D/W. Thin films were dried at room temperature and used for further characterization.

3. Optical study

The thicknesses of Bi_2Se_3 were measured using a surface profilometer. The thickness was found in the range of 630 nm to 910 nm.

The UV-Visible spectrum of as-deposited Bi_2Se_3 thin film was recorded for wavelengths ranging from 500–1100 nm, as shown in Fig. 1(a). In order to determine the band gap of Bi_2Se_3 thin films, the classical absorption equation is used:

$$\alpha h\nu = A(h\nu - E_g)^n. \tag{1}$$

The optical band gap was found to be 1.7 eV with directly-allowed transition, as shown in Fig. 1(b)

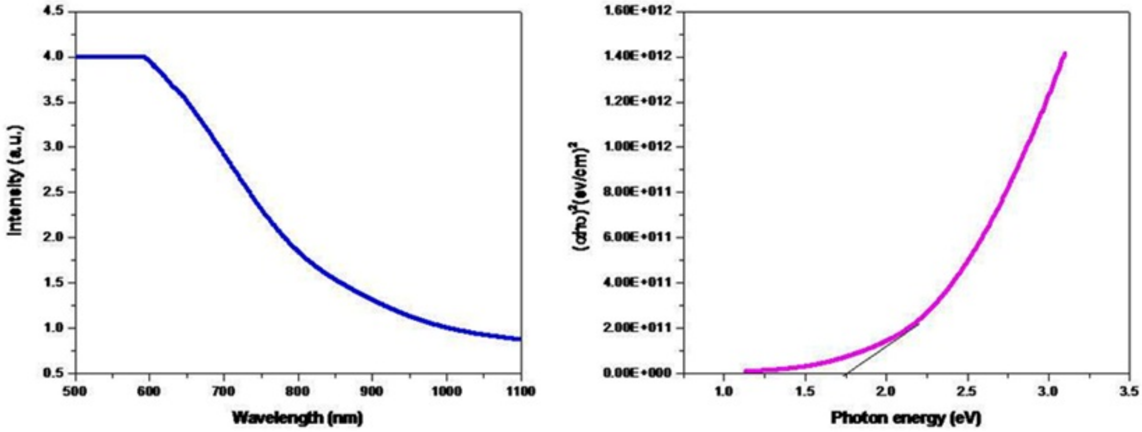

FIG. 1. (a) Optical absorption spectrum of Bi_2Se_3 thin films (b) Plot of $(\alpha h\nu)^2$ vs. $h\nu$

4. Structural study

The phase determination of as-deposited Bi_2Se_3 thin film was done using XRD. All peaks in the XRD pattern are well matched with rhombohedral crystal structure (JCPDS 33-021). The most intense peak is observed at 29.33° for (015) plane. The crystallite size is calculated by the Debye-Sheerer equation.

$$D = 0.9\lambda/\beta\cos\theta. \tag{2}$$

The crystallite size is found to be 47.89 nm.

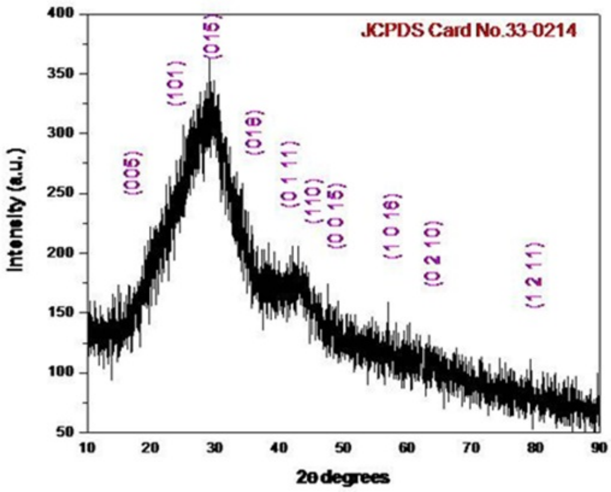

FIG. 2. XRD Patterns of Bi_2Se_3 thin films

5. Morphological and compositional study

The SEM image indicates a uniform, well-adherent and pinhole-free deposition for the Bi_2Se_3 thin film. The SEM micrograph shows an interconnected mesh-like structure.

In order to determine the chemical composition of Bi_2Se_3 thin films, EDS analysis was also carried out. The presence of Bi^{3+} and Se^{2-} was confirmed from EDS. The expected and observed atomic percentages of Bi and Se are in good agreement with standard data. The excess percentage of bismuth is most likely due to an antisite defect. Antisite defects means that excess Bi enters the lattice by replacing Se. The higher percentage of Bi may also attributed to the more metallic character of Bi and its high reactivity towards Se. The small difference in the electronegativity between Bi and Se is also responsible for antisite defect.

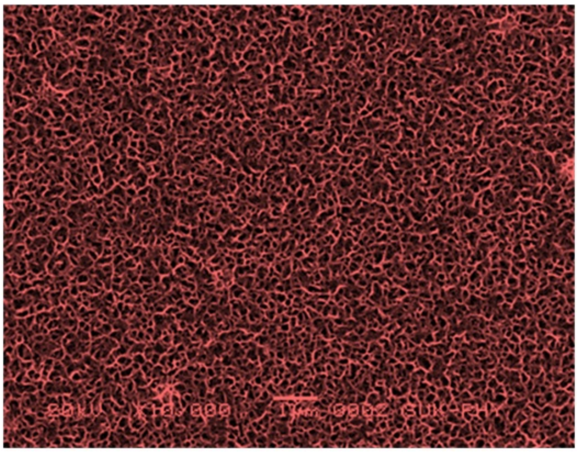

FIG. 3. SEM images of Bi_2Se_3

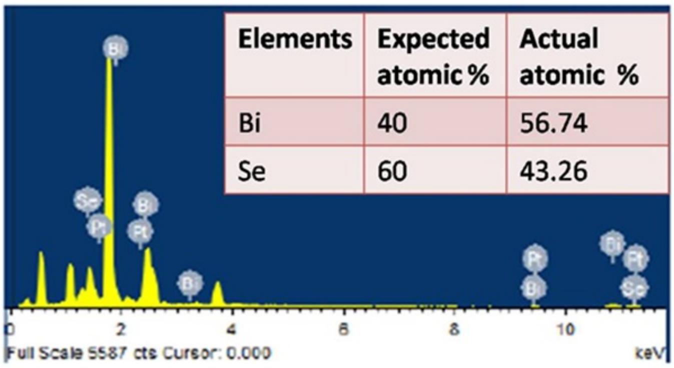

FIG. 4. EDS pattern of Bi_2Se_3 thin films

6. Conclusion

Bi_2Se_3 thin films were synthesized via simple and low cost APT. The optostructural and morphological properties were studied to a film prepared using a surfactant-assisted protocol. The XRD pattern confirmed rhombohedral crystal structure. The SEM pattern revealed an inetrconnected mesh-like structure. The EDS pattern determined the stoichiometric ratio for Bi and Se in the thin film formation.

All these results showed that Bi_2Se_3 thin films may be useful for solar cell application.

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