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# Dielectric and relaxation properties of thermally evaporated nanostructured bismuth sulfide thin films

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ABSTRACT

Nanostructured bismuth sulfide thin films were prepared onto glass substrates with particle size of 21 nm by thermal evaporation using readily prepared bismuth sulfide nanocrystallite powder. The X-ray diffraction pattern revealed that bismuth sulfide thin films exhibit orthorhombic structure. The existence of quantum confinement effect was confirmed from the observed band gap energy of 1.86 eV. AC and DC electrical conductivity of Al/BiSnc/Al structures was investigated in the frequency range 0.5–100 kHz at different temperatures (303–463 K) under vacuum. The AC conductivity ($\sigma_{ac}$) is found to be proportional to angular frequency ($\omega^s$). The obtained experimental result of the AC conductivity showed that the correlated barrier hopping model is the appropriate mechanism for the electron transport in the nanostructured bismuth sulfide thin films. DC conduction mechanism in these films was studied and possible conduction mechanism in the bismuth sulfide thin films was discussed.



## 1. Introduction

In recent years, there is increasing interest on semiconducting nanostructured materials for thermoelectric device applications [1,2]. Particularly, fabrication of nanostructured thin films have opened a novel research in the field of miniaturizing the thermoelectric devices in nano-scale, which offers enhancement in thermo power efficiency, since the materials properties could be easily tuned by the particle size [3,4]. In this context, nanostructured $Bi_2S_3$ thin-films have advocated considerable interest in thermoelectric cooling technologies such as biothermoelectric chip, thermochemistry on a chip, and cooling system for microelectronic components, owing to its high thermoelectric capacity through Peltier effect [5].

Based on these grounds, for integrating thermoelectric film into electronic devices at nano-scale, it is necessary to understand the electrical properties of nanostructured $Bi_2S_3$ thin films. DC conduction studies provide an idea about the conduction of free charges under the application of an external electric field and AC conductivity demonstrates the frequency depended conductivity, where the conduction occurs via trap levels situated in between the band gap of the materials. Various conduction models such as the quantum mechanical tunneling (QMT) [6] and correlated barrier hopping (CBH) model [7] have been proposed to explain the AC conduction mechanism. There are many reports available on the conduction mechanism in inorganic films [8–10], and organic films [11–13] based on metal–semiconductor–metal (MSM) structures. Despite, these investigations, the electrical transport phenomena of nanostructured $Bi_2S_3$ thin films were reported scarce.

Many efforts have been made to prepare nanostructured $Bi_2S_3$ thin films, namely chemical bath deposition (CBD) [14,15], spray pyrolysis [16,17] and electrodeposition [18,19]. However, these films exhibited poor electrical transport property, which limits further research on their thermoelectric properties. Nevertheless, thermal evaporation techniques offer thin film fabrication at large scale with uniform crystallite distribution, which leads to enhancement in thermoelectric power than the chemically prepared films. Nair and co-workers [20] compared the structural and photoelectrical performance of nanostructured $Bi_2S_3$ thin films prepared from CBD and thermal evaporation techniques. Their results revealed that the thermally evaporated films exhibited high photoconduction behavior owing to the highly crystalline and stoichiometry nature than CBD derived films. However, there are not much reports demonstrated on the fabrication of nanocrystalline $Bi_2S_3$ thin films by thermal evaporation technique.

To exploit the processing parameters in thermal evaporation for preparing the $Bi_2S_3$ thin films at nanoscale with uniform crystallite distribution is highly demanding. In our previous reports, we demonstrated the nanostructured CdS [21] and CdSe [22] thin films using thermal evaporation technique (integrated physical–chemical process) by obtaining the material source from wet-chemical technique. Similarly, in the present work we

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prepared nanostructured bismuth sulfide thin films using as-synthesized 1D $Bi_2S_3$ flower-like powder as a source material. Also, we have demonstrated the invoking electrical conduction mechanism in Al/$Bi_2S_3$ nc/Al structures along with the structural and optical properties.

## 2. Experimental techniques

### 2.1. $Bi_2S_3$ powder synthesis

All chemicals were used as received without further purification. Bismuth sulfide powder was prepared by surfactant assisted technique using Triton 100-X as templates. Typical synthesis of bismuth sulfide is as follows: a suspension consisting of bismuth acetate (2 mM) in 20 ml of Triton 100-X (∼24 mmol) was prepared. Aqueous solution of thioacetamide in basic medium was added drop by drop to the above suspension under constant stirring at 80 °C in argon atmosphere. The resulting mixture was refluxed for 12 h in argon atmosphere. After cooling it to room temperature naturally, the black precipitate was collected by filtration. In order to remove the organic residues the product was washed repeatedly with cyclohexane and diethylether to remove the organic residues and finally dried in air at room temperature.

### 2.2. Preparation of bismuth sulfide thin films

Bismuth sulfide thin films of thickness 1000 Å were grown onto pre-cleaned micro-glass slides by thermal evaporation under a pressure of about $10^{-6}$ Torr. The bismuth sulfide powder obtained from surfactant assisted method was used as source material for the preparation of bismuth sulfide thin films. The rate of deposition was maintained at 0.5 nm/s. The thickness of the films were measured using the built-in quartz crystal thickness monitor and was further verified with multiple beam interference (MBI) method.

The structural properties of bismuth sulfide powder and the corresponding thin films were investigated using XRD technique (Rigagu denki-D/Max 2500) equipped with CuKα radiation source. The X-ray tube voltage and current were 40 KV and 100 mA, respectively. Surface morphology analysis was studied by scanning electron microscope (JSM 6400, JEOL, Japan). The composition of the films was examined by OXFORD elemental analyzer. Optical absorption spectra of the films were recorded using SHIMADZU 3101PC UV-VIS-NIR spectrophotometer.

In order to make MSM sandwich (Al/BiSnc/Al) structure, aluminum ohmic electrodes were formed by evaporating pure aluminum (99.9999%) (Sigma Aldrich) on the glass substrates through shadow mask to forms the top and bottom electrode. The dielectric and AC conduction measurements were carried out on the Al/$Bi_2S_3$ nc/Al capacitor using a digital LCR meter (LCR-819, GW Instek, Good Will Instrument company Ltd., Taiwan) in the frequency range 0.5–100 kHz for different temperatures (303–463 K). Digital voltmeters and a digital Pico ammeter (DPM-111- company name) were used for voltage and current measurements, respectively.

## 3. Results and discussion

### 3.1. Structural analysis

Fig. 1(a) and (b) shows the XRD pattern of as-synthesized bismuth sulfide powder and thermally evaporated nanostructured BiS thin films, respectively. The diffraction peaks in Fig. 1(a) reveals polycrystalline nature with pure orthorhombic phase of BiS, which is in good agreement with JCPDS card 17-0320 [23–25]. No diffraction peaks related to Bi, BiOCl and $Bi_2O_3$ were observed. The strong and sharp reflection peaks suggested that the as-synthesized products were well crystallized [26,27]. The average grain size of $Bi_2S_3$ powder was estimated using Debye–Scherer's formula and was found to be 16 nm. The XRD pattern of nanostructured BiS thin films (Fig. 1(b)) revealed the polycrystalline nature with orthorhombic structure of BiS phases. The diffraction peaks marked at 2$\theta$ values correspond to BiS (JCPDS card No. 83-0425). The average grain size of films was estimated by Debye–Scherer's equation using the predominant (0 6 4) peak and was found to be 21 nm.

The morphology of the films was carried out and resultant SEM image is presented Fig. 1(c). From Fig. 1(c) it reveal that the film have uniform and smooth granular surface, where the crystallites are in nanoscale between ∼30 and 40 nm. When comparing the crystallite size with XRD analysis (21 nm) small discrepancy was existed, this attributed to the negligence of peak shift due to substrate strain in Debye–Scherer's relation. The large crystallites found in the films surface may originate from the coalescence of smaller grains.

### 3.2. Optical analysis

The variation of optical absorption coefficient with wavelength was studied using optical absorption spectra, which provide the nature of the electronic transition across the optical band gap. The nature of the transition was determined by using the relation [28]

$$\alpha = \frac{A(h\nu - Eg)^n}{h\nu} \quad (1)$$

where $A$ is a constant, where $n = 1/2$ for allowed direct transition and $n = 2$ for indirect transition.

The absorption coefficient $\alpha$ is calculated using the relation, $\alpha = 4\pi k_f/\lambda$. Where $k_f$ is the extinction coefficient estimated from $(2.303\lambda \log(1/T_0))/(4\pi t)$. $T_o$ is the transmittance of the films and '$t$' is thickness of the films (1000 Å) [29]. The transition nature was verified with each cases ($n = 1/2$ and $n = 2$) and it satisfied with $n = 1/2$. The plot of $(\alpha h\nu)^2$ vs $h\nu$ and $(\alpha h\nu)^{1/2}$ vs $h\nu$ shown in Fig. 2(a) and (b), respectively. The straight portion is extrapolated to the energy axis, and when $(\alpha h\nu)^2 = 0$, the intercept gives the band gap energy of $Bi_2S_3$. The estimated optical band gap was found to be 1.64 eV ± 0.4 eV, and 1.31 eV ± 0.4 eV for direct and indirect transisition, respectively. In order to verify the onset of absorption (the edge of minimum reflectance/maximum absorption) diffused reflectance spectra were demonstrated (Fig. 2(c)). The band edge has been observed at 1.64 eV from Fig. 2(c) is comparable to direct transition (Fig. 2(a)). The estimated absorption coefficient values are in the range of $10^7$. This is apparently higher than that of reported values (∼$10^4$–$10^5$) those films derived by chemical bath deposition [30,31]. The high absorption coefficient of 1000 Å films may ascribe to high compact nature of films by thermal evaporation process when compare to chemical bath deposited films. The observed nanocrystallite growth in bismuth sulfide films may ascribe to temperature gradient condition exhibits during thermal evaporation [32].

### 3.3. Electrical conduction analysis

#### 3.3.1. Temperature and frequency dependence of A.C conduction studies

The AC conductivity ($\sigma$) of nanostructured BiS thin films was measured as a function of frequency and temperature. Fig. 3(a) demonstrates the dependence of the conductivity on frequency (0.5–100 kHz), at different temperatures on a log–log scale. It is observed that the conductivity gradually increases with increases in frequency and temperature. For the range of temperature