Improved Optoelectronic Properties of Nanostructured Eu Doped Bi$_2$S$_3$ Thin Films for the Detection of UV Light

Mohd Shkir 1,2, Amira Ben Gouider Trabelsi 3,*, Fatemah H. Alkallas 3, Salem AlFaify 1, Bidhan Pandit 4 and Mohd Ubaidullah 5

Abstract: Due to a suitable band gap and high light absorption behavior, Bi$_2$S$_3$ is showing major success in photo-to-current conversion applications. In this current work, the authors used a low-cost nebulizer spray pyrolysis method to create nano-sized pure and unique Eu contents (1–5 wt.%)-loaded Bi$_2$S$_3$ thin layers by taking bismuth nitrate and thiourea as the source materials. The parent and Eu doped Bi$_2$S$_3$ thin films, deposited on a well-cleaned glass substrate at 350 °C, were analyzed using a variety of characterization approaches, including FESEM, EDS, XRD, PL, UV-Vis, and I-V, to describe the morphologies, compositions, crystallinity, defect states, band gap, and photodetection capability, respectively. The X-ray diffraction outcomes confirmed an orthorhombic polycrystalline structure for all Eu concentrations, and they were highly oriented along the (130) plane. Incorporation of Eu into the host matrix improves the intensity of all the peaks, and the crystallite size (25 nm) was found to be highest for the 3% Eu doped Bi$_2$S$_3$ thin film. The formation of a nanowire-like morphology was confirmed thorough field emission electron microscopy analysis, which is preferred for photo detectors. Upon excitation at 325 nm, grown pure and Eu doped Bi$_2$S$_3$ thin films indicated five emission peaks at 387, 418, 439, 480, and 523 nm, respectively. All the films showed significant absorption in the UV region, and importantly, a narrowing of the band gap is seen from 2.29 to 2.17 eV. Finally, the current-voltage characteristics of the pure and Eu doped Bi$_2$S$_3$ thin films were tested using silver contacts as electrodes. The results showed that the 3% Eu doped Bi$_2$S$_3$ sample showed a higher UV photocurrent characteristic, with high specific detectivity (1.82 × 10$^{10}$ Jones), photoresponsivity (3.88 × 10$^{-1}$ AW$^{-1}$), external quantum efficiency (125%), and rapid photo response, as well as a recovery speed of 0.3 s and 0.4 s, due to the effective light absorption and photocarrier generation. We believe that our study may provide a cost-effective approach for UV photosensor applications.

Keywords: Eu loaded Bi$_2$S$_3$ thin layers; nebulizer spray pyrolysis; nanowire; narrowing band gap; higher UV photo response

1. Introduction

In recent years, modern academic and industrial researchers have expended tremendous research efforts for technological advancement in the fields of electronics and optoelectronics due to their excellent applications. There is no doubt that photosensors or photodetectors are the lifeblood of the optoelectronic industry, as they converts absorbed photons into electrical signals via electron–hole pair creation. Recently, the research hotspot has turned to finding low cost as well as non-toxic photosensing semiconductor materials.
in the form of nanostructures with appropriate electrical and optical properties, especially in the form of thin films, as they exhibit notable advantages, such as fewer material requirements and ease of application on different substrates. Photosensitive materials derived in the form of nanostructures (nanobelts/nanorods/nanotubes/nanowires) exhibit excellent photo-current properties, with a rapid response rate due to their superior properties such as a large surface area to volume ratio, which improves the absorption level and quantum size effect [1,2]. Precisely, researchers hold great consideration for nanorods, thanks to their electron–hole separation efficiency and the migration of their charge carriers [3,4]. Moreover, nanorods are always very sensitive to light and gas. Besides that, they can be applied in various sophisticated applications, including piezoelectric nanogenerators, lithium-ion batteries, optical interconnections, medical diagnostics, and optical switches [5]. As mentioned above, the fabrication of low cost, environmentally friendly, and easy to process photosensing nanorod materials with high a photocurrent, as well as good reponsivity, detectivity, external quantum efficiency, and stability are required to fulfill the next generation goals. Currently, metal-based semi-conducting chalcogenide materials with a typical formula of $A_2B_3$ have sparked great interest in the field of low-cost energy conversion applications due to its suitable electrical and optical properties [6]. Out of numerous metallic sulfides, orthorhombic bismuth trisulfide, or bismuth sulfide ($\text{Bi}_2\text{S}_3$), is one of the unique and technologically important materials in V-VI semiconductors. It has become one of the hot topics as a favorable material in the study of photosensors due to its great electron mobility, optimum band gap (1.3–1.7 eV), super wide high optical absorption co-efficient ($10^4$–$10^5 \text{ cm}^{-1}$), notable light-current conversion efficiency (~5%), good redox chemistry character, easiness in synthesis, lower price, easy deposition on different substrates, massive availability, good conductivity, and stability [7–9]. It is attracting increased attention because of its conduction band (CB) edge position and nontoxic nature compared to other metal sulfides (Cd, Pb, Hg) [10]. An extra advantage of this sulfide and bismuth material is abundance in the earth. Moreover, the trivalent bismuth sulfide ($\text{Bi}^{3+}$) is found to be n-type in nature, mostly due to large number of sulfur vacancies which effectively tune various physio-chemical properties of this material [8], making as a useful material for solar selective coating, supercapacitor electrodes, photodiode arrays, thermoelectric devices, and pigments [11]. It is noteworthy that the presence of sulfur vacancy in the $\text{Bi}_2\text{S}_3$ material supports the generation of defect centers, which induces the transfer of carriers from the valance band. This transfer of carriers and defect centers may enhance the electron–hole pair creation and an excess electron–hole can play vital role to boost the photosensitivity of the material [6].

Xiao et al. [12] synthesized of bismuth sulfide ($\text{Bi}_2\text{S}_3$) with various hierarchical architectures and studied their photosensing properties. Desale et al. [13] studied the photosensing response of the SILAR prepared $\text{Bi}_2\text{S}_3$ thin films by annealing. The annealed sample (at 250 °C) shows a higher photocurrent ($1.75 \times 10^{-9} \text{ A}$) and photosensitivity (61%) than the parent sample. Arumugam et al. [5] manufactured a nanowire $\text{Bi}_2\text{S}_3$ based photosensor. In their research, they studied the photosresponse of the $\text{Bi}_2\text{S}_3$ material by changing the doping concentration of Ag (1, 3, and 5%). According to their results, the 1% Ag doped $\text{Bi}_2\text{S}_3$ sample exhibited a high photocurrent $1.51 \times 10^{-3} \text{ A}$ at an applied voltage of 1 V. The chemical bath deposition technique of Shaikh Shaheed et al. [14] prepared CdSe-$\text{Bi}_2\text{S}_3$ bi-layer thin films on ITO glass substrates, demonstrating the high photosensitivity of 0.54. No study was made on the other essential parameters, such as detectivity and external quantum efficiency. Recently Wei et al. [15] synthesized Ho doped $\text{Bi}_2\text{S}_3$ film, and the nano flake-like structure increased the photocurrent from 0.366 to 1.09 mA/cm$^{-2}$. The increased photocurrent was attributed to its increased number of photo-generated carriers, the reduction in the band gap, and the nanostructure morphology. However, the photocurrent properties of the currently available $\text{Bi}_2\text{S}_3$ based photosensor are not meeting the practical requirements. This may limit the commercial applications of the photosensor. Therefore, room for improvement in the photosensing properties of $\text{Bi}_2\text{S}_3$ still exists. This fact is forcing the research community to solve these issues. To obtain a high performance
photodetector, many researchers considered the incorporation of rare earth metal ions as the most effective and fastest potential approach because they have the ability to act as effective luminescence centers (due to their 4f-4f transitions), as well as to provide bandgap tuning and photoionization transitions via radiative or nonradiative decay, which may induce photoresponse activity [16]. Additionally, rare earth elements have several advantages, including high environmental safety and good thermal and isotopic stability [2]. Wei et al. [15] determined that the doping of rare earth element will definitely alter the band gap of the parent material. Particularly, europium ions (Eu$^{3+}$) can be incorporated into the Bi$_2$S$_3$ matrix, thanks to its band gap modification ability, sharp luminous qualities with different energy levels, longer optically active state lifetimes, and ionic size (Eu$^{3+}$ = 0.95 Å) closer to that of bismuth (Bi$^{3+}$ = 0.103 nm) [17–19]. The close ionic radii can easily replace Bi$^{3+}$; as a result, electronic structures and structural quality can be easily altered. Hasabeldaim et al. [20] mentioned that the well-known red emission property of europium has the ability to enhance optoelectronic properties. Thus far, Mohd Shkir et al. [18], Arulanantham et al. [21], and Devi et al. [22] have recorded excellent photosensing results for chalcogenide based materials (SnS$_2$:Eu) (CdS:Eu) (ZnS:Eu) via Eu as a dopant. The abovementioned survey revealed the role of Eu in boosting the photocurrent properties. Plentiful synthesis approaches were followed to obtain nanostructured (nanoflowers, nanotubes, nanonetwork, nanoribbons, nanorods, etc.) bismuth(III) sulfide thin films [23,24]. Compared with the other techniques, the solution-based nebulizer-assisted spray pyrolysis technique is the most convenient method to obtain various types of nanostructures with minimal material loss. This enables one to fabricate stoichiometric, high quality, good crystallinity, pinhole free, and inexpensive large-scale thin film devices (with the required properties) over massive areas of substrates [25]. In this current study, we report for the first time nebulizer spray pyrolysis-deposited 1, 3, and 5% Eu doped Bi$_2$S$_3$ thin film fast photoresponse applications, as well as study their structural, morphological, and optical properties with respect to the dopant concentration.

2. Materials and Instrument Details

In this work, we took bismuth nitrate (Bi$_2$(NO$_3$)$_2$), thiourea (CS(NH$_2$)$_2$), and europium nitrate (Eu(NO$_3$)$_3$·5H$_2$O) to develop pure and Eu doped Bi$_2$S$_3$ thin films; all of these were sourced from Sigma Aldrich. For preparing samples, no additional purification was performed. In detail, for preparing pure Bi$_2$S$_3$ thin film, the base solutions or precursor solution were prepared by dissolving 0.03 M of bismuth nitrate and 0.05 M of thiourea in 10 mL of double distilled (D.D.) water and constantly stirring for nearly 25 min under the normal atmospheric environment to yield a homogeneous mixture. Finally, the mixture solution was subjected to spraying on a well-cleaned glass substrate, and its temperature was set at 350 °C. To achieve doping, the above solution was mixed with different (1, 3, and 5%) weights of europium nitrate. The selected glass substrates were well cleaned by washing with a soap solution, hot chromic acid, and acetone in succession, along with hot distilled water. The other coating parameters of the nebulizer spray pyrolysis system, such as substrate to spray nozzle distance and pressure, were maintained at 4 cm, and 1.5 kg/cm$^2$, respectively. At last, the system was turned off and all the deposited samples were allowed to cool naturally before collection to check the structural, morphological, and photo current properties.

To check the phase and the orientation of the undoped and Eu doped Bi$_2$S$_3$ films, the XRD profiles were recorded via a PANalytical X’Pert Pro X-ray diffractometer with CuK$\alpha$ radiation ($\lambda$ = 1.5406 Å), FE-SEM Thermo scientific Apreo S, Waltham, MA, USA was utilized to scan the surface morphology and to prove the presence of certain elements of the readied samples. The types of defect levels and intensity of emissions were acquired using a Perkin Elmer LS-55 fluorescence spectrometer at an excitation of 325 nm. The optical data of the coated films were acquired through a double-beam UV-VIS-NIR spectrophotometer (Lambda Perkin Elmer, Waltham, MA, USA). Dark and light I-V studies of the Bi$_2$S$_3$: Eu...
coated samples were performed through a Keithley electrometer (Model-2450) by applying voltage in the range of ±5 V.

3. Results and Discussion

3.1. Structural Analysis

To explore the phase purity, as well as the crystalline constitution of the synthesized pure and Eu doped Bi$_2$S$_3$ films, and to determine whether the chosen dopant element in the current work effectively yielded high-quality films, XRD analysis was carried out at room temperature. Figure 1 allows for identification of the changes in Bi$_2$S$_3$ crystalline quality with respect to the diverse amount of Eu concentration. Two well-defined Bragg reflections belonging to the (130) and (221) planes and thirteen tiny Bragg reflections indexed to the (020), (210), (101), (021), (320), (410), (240), (041), (411), (440), (501), and (312) planes were originated from the conventional orthorhombic formation of Bi$_2$S$_3$, and they have the same appearance as JCPDS No. 43-1471 [26]. According to the results, the (130) peak is the dominant peak for both the undoped and doped samples. The greater number of strong and narrow peaks show the polycrystalline and good crystallinity of the samples. From this observation, all the samples displayed similar diffraction peaks as to those exhibited by the undoped sample. However, the inserted Eu element amplified the strength of the peaks steadily up to 3%, and above 3%, it affects the quality of the peaks due to lattice distortion. Further, we noticed that the crystalline quality directly depends on the amount of dopant concentration, and the 3% Eu doped Bi$_2$S$_3$ thin film sample has the highest crystalline nature. This suggests that the Eu element can easily replace the bismuth atom, owing to its close ionic radii, amplifying its crystallinity. However, for higher concentrations (5% Eu), it can only occupy at interstitial sites of bismuth, resulting in the decrease in crystallinity. Since no Eu related peaks are seen in the XRD profile, this proves the successful replacement of the bismuth atom by the Eu element in the synthesized samples. It is noteworthy that high crystalline quality is one of the basic parameters which helps to increase the photosensing properties [27].

Figure 1. XRD pattern of un-doped and Eu doped Bi$_2$S$_3$ thin films.
It is well known that a material’s current conduction property mainly depends upon mean crystallite size. The Debye–Scherrer empirical equation [28] was applied to the most influential diffraction peak (130) to compute the mean crystallite size and the existing microstrain of the nano-crystallites Bi$_2$S$_3$ thin films. The computed results are reported in Table 1.

$$D = \frac{0.9 \lambda}{\beta \cos \theta}$$  \hspace{1cm} (1)

$$\varepsilon = \frac{\beta \cot \theta}{4}$$  \hspace{1cm} (2)

where D is average crystalline size, and $\varepsilon$, $\lambda$, $\beta$, $\theta$ stand for micro strain, X-ray wavelength, full width of the dominant (130) peak, and the peak Bragg’s angle, respectively.

Table 1. Crystallite size, strain, lattice constants, and cell volume of the Eu doped Bi$_2$S$_3$ thin films.

| Samples          | Crystallite Size (nm) | Strain $\times 10^{-3}$ | Lattice Constant | Cell Volume ($Å^3$) |
|------------------|-----------------------|--------------------------|-------------------|--------------------|
| Bi$_2$S$_3$      | 21                    | 7.46                     | 11.254            | 3.9690             | 11.099 | 496.0 |
| Bi$_2$S$_3$:Eu1% | 24                    | 6.73                     | 11.258            | 3.974              | 11.120 | 497.6 |
| Bi$_2$S$_3$:Eu3% | 25                    | 6.28                     | 11.265            | 3.975              | 11.115 | 497.7 |
| Bi$_2$S$_3$:Eu5% | 19                    | 8.29                     | 11.277            | 3.976              | 11.133 | 499.2 |

The computed crystallite size for pure and Bi$_2$S$_3$: Eu (1, 3, and 5%) thin films are 21, 24, 25, and 19 nm, respectively. As a consequence of Eu dopant, the crystallite size was found to be improved, and the sample made with a 3% Eu has the largest crystallite size of 25 nm, which is expected to display better photosensing results. The reason is that the large grain size can increase the absorption of the coated sample, which may help to increase light-current properties by generation of the electron–hole pair [29]. The other possible reason is that the larger grains reduce the grain boundaries, easing the electron transformation. The micro strain developed in the films is lessened from $7.46 \times 10^{-3}$ to $6.28 \times 10^{-3}$, and it was the smallest for 3% Eu doped Bi$_2$S$_3$ thin film. This implies that the dopant and parent materials stabilize the surfaces/grain boundaries and resist the formation of different types of deforming forces. This indicates the reduction of crystal misalignment or crystal imperfections. This verifies the formation of high quality superior films [30]. Recently, Devi et al. [22] observed a similar kind of crystallite size and strain variation for improved photosensing.

To study the doping fraction insertion, the lattice parameters ($a$, $b$, $c$) and cell volume of orthorhombic Bi$_2$S$_3$ thin films were estimated using the following equations, as presented in Table 1.

$$\frac{1}{d^2} = \left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}\right)$$  \hspace{1cm} (3)

$$V = abc$$  \hspace{1cm} (4)

The estimated values of the lattice parameter for pure Bi$_2$S$_3$ thin film is $a = 11.254 Å$, $b = 3.9690 Å$, and $c = 11.099 Å$, which fit well with those in previously reported works [13,31]. As a consequence of the Eu element, one can observe that the lattice parameter and cell volume values are expanded. This expansion, which developed in the Eu doped Bi$_2$S$_3$ thin films, can be due to the difference between the ionic radii (Eu$^{3+} = 0.95 Å$) (Bi$^{3+} = 0.103$ nm) and the strains developed in the samples [32].

### 3.2. Morphology Studies

The FE-SEM photographs (Figure 2) were taken to assess the dopant impact (0, 1, 3, and 5%) on the surface structure and morphology of the Bi$_2$S$_3$ films; these are provided in Figure 2a–d. From the results, we noticed a continuous variation in the surface nature due to the dopant element. The parent Bi$_2$S$_3$ thin film consisted of closely packed rod-like
uniform grains, which were grown nearly vertically to the glass substrates. Usually, this kind of rod-like grains facilitates charge separation due to the least diffusion distance [10]. Yue Wang et al. [33] recorded a rod-like nanostructure for spray-coated Bi$_2$S$_3$ thin films. When the dopant content increases to 3%, an uneven/irregular nanorod is noted, and the length as well as diameter of the nanorod is increased. On the other hand, in the case of Bi$_2$S$_3$: Eu (5%), the formation of a nanorod structure has almost vanished. It is worth noting that the density of nanorods per unit area is high for the Bi$_2$S$_3$: Eu (3%) sample. This property is vital, as it can reduce current leakage and promote the mode of electron flow, as well as photon absorption ability due to increased surface area [30,34]. Therefore, these results can allow the Bi$_2$S$_3$: Eu (3%) sample to yield better photodetection results.

Figure 2. FESEM images of Eu-doped Bi$_2$S$_3$ thin films with different Eu concentrations (a) 0%, (b) 1%, (c) 3%, and (d) 5%.

Further, to understand the purity of the Bi$_2$S$_3$ samples, Energy Dispersive X-ray spectrum (EDX) images were obtained. Figure 3, showing the Bi$_2$S$_3$: Eu (3%) sample, specifies the presence of required elements such as Bi, S, and Eu. The attained spectrum proves the purity of the coated sample.

3.3. Photoluminescence (PL) Analyses

To further investigate the fate of the electron–hole pairs, photoresponsive sites, band gap energy, and defects present in the spray coated Eu doped Bi$_2$S$_3$ thin films, photoluminescence spectroscopic analysis is useful. The PL emission spectra (350–600 nm) of all the readied Bi$_2$S$_3$ samples are presented in Figure 4. As is seen in Figure 4, upon excitation at 325 nm (3.81 eV), the coated samples featured four distinct photoresponsive emission bands around 400 nm (3.1 eV), 427 nm (2.9 eV), 459 nm (2.7 eV), 482 nm (2.57 eV), and
516 nm (2.4 eV) nm. The first band appeared around 400 nm (3.1 eV), which might be because of the band-to-band emission, or band edge luminescence, that arises from the recombination of the excitons [35]. The second, third, and fourth peaks around 427 nm (2.9 eV) and 459 nm (2.7 eV), and existing in the violet region, are associated defects related to Bi and S [36]. The final green emission peak identified at 516 nm (2.4 eV) is a characteristic high-level transition of Bi$_2$S$_3$ nanocrystallites which appears due to trapped electron–hole pairs recombination [26]. Compared to the parent sample, the PL intensity is increased with increasing Eu$^{3+}$ content, reaching high intensity for the 3% Eu doped Bi$_2$S$_3$ sample. Finally, the intensity drops for higher concentrations, i.e., the 5% Eu doped Bi$_2$S$_3$ sample. The high intensity indicates the higher recombination rate of the electron–hole pairs, increasing the surface area and crystallinity of the sample. This improvement in the crystallinity reduces the defects and raises the recombination of the excitons. It has been reported that these results can increase UV emissions [20]. On the other hand, the increased surface area of the sample subjected to the photon source will effectively improve the light absorption and charge carrier generation [37,38]. Further, it is seen that the addition of Eu content redshifts the peaks, which can cause the band gap of the sample to decrease.

![Figure 3. EDX spectrum of 3% Eu-doped Bi$_2$S$_3$ thin film.](image)

3.4. Optical Studies

The detailed photoabsorption and approximate energy band gap of the readied Bi$_2$S$_3$:Eu thin layers were documented between the wavelength range of 300–900 nm. The recorded UV/visible absorbance profiles are collectively given in Figure 5a. It is evident from Figure 5a that all the coated Bi$_2$S$_3$ thin layers displayed strong optical response in the UV regime, which is essential for UV photoreponse performance. As the dopant element enters into the parent material, the light absorption seemed to increase in the UV region, turning to drops after 400 nm. The Bi$_2$S$_3$: Eu (3%) featured the highest light absorption intensity over the other samples. This might be due to high grain size of the sample. The large grain size scatters the incident beam in all directions, and clearly enriches...
the light absorption ability [2,39]. The superlative light absorption ability can induce more
carrier generation, which is considered as urgent for the photosensor. Thus, the
coated Bi$_2$S$_3$: Eu (3%) can provide significant UV photosensing performance.

Figure 4. Photoluminescence spectra of Eu-doped Bi$_2$S$_3$ thin films with different Eu concentrations.

From the photoabsorption profile, the optical energy band gaps of both Bi$_2$S$_3$ and Eu
doped Bi$_2$S$_3$ thin films were estimated using the well-known Tauc’s relation [26]

$$a h\nu = A (h\nu - E_g)^{1/2}$$

where $E_g$, $h\nu$ denotes optical band gap and incident photon energy, and $a$, $A$ represents
absorption coefficient and proportionality constant respectively. The optical band gap is
extracted from the plots $h\nu$ vs. $(a h\nu)^2$, which are shown in Figure 5b. In this work, the
estimated band gaps of Bi$_2$S$_3$: Eu (0%), Bi$_2$S$_3$:Eu1%, Bi$_2$S$_3$:Eu3%, and Bi$_2$S$_3$:Eu5% are 2.29,
2.21, 2.17, and 2.28 eV. It is important to underline that the band gap is found to drop down,
reaching its lowest level for Bi$_2$S$_3$: Eu3% thin film. The smallest band gap sample Bi$_2$S$_3$: Eu (3%) can easily complete the charge transfer process throughout the sample, which is
beneficial for the photodetector. It is worth mentioning that the following factors, such as
stoichiometry deviation, high photon-absorption level, orientation, and increased particle
size of the sample, can reduce the band gap energy of the coated samples [2,40]. In the
present case, the decrease in band gap is due to increased particle size and the generation
of defects and disorder in the Bi$_2$S$_3$ lattice, which allow for the formation of localized states and deep levels in the band gap.

![Graph showing absorption spectra and Tauc plots](image.png)

**Figure 5.** (a) Absorption spectra and (b) Tauc plots of Eu-doped Bi$_2$S$_3$ thin films with different Eu concentrations.

3.5. Photocurrent Studies

Finally, the light current properties (dark current ($I_d$) and photocurrent ($I_{ph}$)) of the present Bi$_2$S$_3$ nanorods for different weight percentages, recorded at room temperature in the presence of dark and light modes (365 nm) by applying constant bias voltage, ranges...
from −5 to +5 V. To make a photosensor, the deposited samples were taken in an area of 1 cm × 1 cm and silver paste was applied over the film to create working electrodes. The schematic depiction of the fabricated UV photosensor based on the Bi2S3 thin films is given in Figure 6. The plotted current variations, as a function of bias voltage (current-voltage (I−V)) characteristic of the present samples, are showed in Figure 7. Before measuring the dark current, the coated samples were kept in a dark state for about 10 h. The obtained dark current and photocurrent exhibit good linear trend characteristics as the applied voltage increases, suggesting the excellent formation of an ohmic junction between the Ag electrode and Bi2S3:Eu thin films. Under the light mode, a higher current is realized for all the samples, which proves the current ability of the present coated samples. The dark current of the Bi2S3: Eu (0%), Bi2S3: Eu (1%), Bi2S3: Eu (3%) and Bi2S3: Eu (5%) is 0.7 × 10−6, 0.4 × 10−6, 0.3 × 10−6, and 1 × 10−6 A, respectively. The observed dark current is very small, which is a necessary condition for an efficient photosensor. This dark current will improve the detection performance. With the increase in the Eu doping concentration, the light current gradually increases from 1.2 × 10−6 A to 21 × 10−6 A, attaining a maximum value of 21 × 10−6 A for Bi2S3:Eu the 3% sample under the same illumination conditions. These interesting responses of the Bi2S3:Eu3% sample are mostly related to the good structure and film quality, low defect density, increased separation of electron–hole pairs, less recombination of charge couples, good ohmic contact of the Ag and Bi2S3 thin film, reduced band gap (which allows for the absorption of more photons), and increased crystallite size, which reduces the grain boundary, causing improvement in the electrical conductivity [25,40,41].

Apart from the cost of the photosensor, understanding the three most essential parameters, i.e., photoresponsivity (R), detectivity (D∗), and external quantum efficiency (EQE) of the light detector is vital, and they were calculated using the given equations (Equations (6)–(8)). The calculated R, D∗, and EQE values of the presented Bi2S3: Eu samples are given in Figure 8.

\[
R = \frac{I_p}{P_m} \times A \quad (6)
\]

\[
D^* = R \sqrt{\frac{A}{2eI_d}} \quad (7)
\]

\[
EQE = R \frac{hc}{e\lambda} \quad (8)
\]

Figure 6. The schematic depiction of the fabricated UV photosensor.
Figure 7. Semi-log I–V characteristics of the fabricated Eu-doped Bi$_2$S$_3$ photosensor measured under dark and illuminated conditions at a bias voltage between $-5$ and $+5$ V, prepared using different Eu doping concentrations.

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$$R = \frac{I_{\text{ph}}}{P_{\text{in}}} \cdot A$$

$$D^* = \frac{R}{A^2 \epsilon I_{\text{d}}}$$

$$\text{EQE} = \frac{R \ h \ c}{e \ \lambda}$$

The parameters $A$, $I_{\text{ph}}$, $P_{\text{in}}$ stand for the active sensitive area of the sample, the photo-current, and power of the light source, while the symbols $\lambda$, $e$, $I_{\text{d}}$, $h$, and $c$ denote the wavelength of incident light, electron charge value, dark current, Planck's constant, and velocity of light, respectively. The plotted graph (Figure 8) reveals that the Bi$_2$S$_3$: Eu (3%) sample displayed better $R$ ($3.88 \times 10^{-1}$ AW$^{-1}$), $D^*$ ($1.82 \times 10^{10}$ Jones), and EQE (125%) values than the other coated samples.

Figure 8. Responsivity, detectivity, and external quantum efficiency of the Eu-doped Bi$_2$S$_3$ photosensor, with Eu doping concentrations.

We conducted further research on the time-dependent key factors, i.e., the detection speed (response time and recovery time) of the present photodetector with respect to the ON/OFF light source at 5 bias voltage. The temporal photoresponse plots of the presented Bi$_2$S$_3$: Eu samples are shown in Figure 9. When the UV light was turned on, the photocurrent response of the samples shows dramatic enhancement, with rapid saturation. A sharp fall to the initial dark current value is noted when the light is switched off. This indicates the steady switching behavior of the prepared samples. The recorded rise/fall speed of the Bi$_2$S$_3$: Eu (0%), Bi$_2$S$_3$: Eu (1%), Bi$_2$S$_3$: Eu (3%), and Bi$_2$S$_3$: Eu (5%) thin films were found to be in the order of $2.6/2.8$ s, $1.3/1.4$ s, $0.3/0.4$ s, and $0.4/0.4$ s, respectively. The recovery time of all the samples is observed to be slightly lower than the response speed, and the Bi$_2$S$_3$: Eu (3%) thin film displayed the lowest value of rise/decay time compared to the other deposited samples, which proves the high detection speed of the sample. The fast rise and fall times of Bi$_2$S$_3$: Eu (3%) thin film is owing to the rapid electron–hole pair generation and recombination rate. Generally, the nanorods have a high surface-to-volume ratio and will act as recombination centers for the charge carriers, leading to a rapid rise/fall time [4].
The parameters $A$, $I_p$, $P_{in}$ stand for the active sensitive area of the sample, the photocurrent, and power of the light source, while the symbols $\lambda$, $e$, $I_d$, $h$, and $c$ denote the wavelength of incident light, electron charge value, dark current, Planck’s constant, and velocity of light, respectively. The plotted graph (Figure 8) reveals that the Bi$_2$S$_3$: Eu (3%) sample displayed better $R$ ($3.88 \times 10^{-1}$ A W$^{-1}$), $D^*$ ($1.82 \times 10^{10}$ Jones), and EQE (125%) values than the other coated samples.

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![Figure 9](image-url)

**Figure 9.** Plots of current vs. time of Eu-doped Bi$_2$S$_3$ photosensor using different Eu doping concentrations.

In this section, we compare the performance of the previously reported literature with the currently developed photosensor for a better and more clear understanding of the current study; the compared performance parameters are listed in Table 2.

Veeralingam et al. [42] manufactured Bi$_2$S$_3$ microneedles/RuS$_2$ nanorods, and
the heterostructure formation shows the maximum responsivity of $39 \times 10^{-3}$ A/W. Paulraj et al. [43] observed a high responsivity value of 0.29 AW$^{-1}$ for an Sm doped Zns photosensor developed via the nebulizer spray technique. Shaikh et al. [44] annealed a CdS–Bi$_2$S$_3$ heterojunction photodetector which exhibited notable photosensitivity of 0.43 A/W. The Bi$_2$S$_3$/rGO heterojunction based photosensor synthesized by Ladan et al. [45] displayed a rapid response/recovery speed of 175/401 s. Recently, Jesu et al. [46] fabricated nebulizer sprayed Cu doped ZnS thin films that showed notable R ($2.24 \times 10^{-2}$ AW$^{-1}$), D* ($2.66 \times 10^{10}$ Jones), and EQE (7.23%) values. Rajeswari et al. [26] also coated Fe doped Bi$_2$S$_3$ samples, displaying reasonable parameter values of $R = 9.60 \times 10^{-2}$ AW$^{-1}$, $D^* = 1.34 \times 10^{10}$ Jones, and EQE = 22.4%, with a rapid rise/fall speed of 0.3/0.4 s. The photosensing data of the present Eu doped Bi$_2$S$_3$ sample is higher than these previously reported values.

Table 2. Comparison of the photosensor parameters of the current work with the previous sulfide-related photodetectors.

| Sample          | Responsivity (AW$^{-1}$) | External Quantum Efficiency (EQE) (%) | Detectivity (Jones) | Rise Time (s) | Fall Time (s) | Ref. |
|-----------------|--------------------------|--------------------------------------|---------------------|---------------|---------------|------|
| Bi$_2$S$_3$     | $39 \times 10^{-3}$      | -                                    | -                   | 0.6           | -             | [42] |
| PbS:Sm         | 0.29                     | -                                    | -                   | -             | -             | [43] |
| CdS/ Bi$_2$S$_3$| 0.43                     | -                                    | -                   | -             | -             | [44] |
| Bi$_2$S$_3$/rGO| -                        | -                                    | -                   | 175           | 401           | [45] |
| ZnS:Cu         | $2.24 \times 10^{-2}$    | 7.23                                 | $2.66 \times 10^{10}$| 1             | 3             | [46] |
| Bi$_2$S$_3$:Fe | $9.60 \times 10^{-2}$    | 22.4                                 | $1.34 \times 10^{10}$| 0.3           | 0.4           | [26] |
| Bi$_2$S$_3$:Eu | $3.88 \times 10^{-1}$    | 125                                  | $1.82 \times 10^{10}$| 0.3           | 0.4           | Present work |

The three possible phenomena behind the photoresponse mechanism of the manufactured Bi$_2$S$_3$ photodetector are photon absorption, photocurrent generation, and transport of the photocarriers. On the other hand, the photoresponse is mainly achieved by the adsorption and desorption of oxygen molecules, which modify the photocurrent production. Under dark conditions, the adsorption of oxygen molecules on the top surface of the samples received the negatively charged ion ($O_2^- + e^- = O_2$). This process widens the depletion layer. When UV light falls on the surface of the Bi$_2$S$_3$ sample, its energy is absorbed, and electron–hole pairs are produced. The holes produced during light absorption discharge the negatively charged ion ($h^+ + O_2^- \rightarrow O_2$). This effect makes the depletion layer very thin, causing the charge carriers to easily penetrate the layer, causing an increase in the photocurrent. This process is described in Figure 10.

Figure 10. Mechanism of the photoconductivity of the Bi$_2$S$_3$ thin film.
4. Conclusions

In summary, for the first time, we have prepared a low-cost, easy, nontoxic, and highly UV sensitive pure Bi$_2$S$_3$, as well as an Eu 1–5 wt.%-doped Bi$_2$S$_3$ thin film on a cleaned glass substrate. The incorporation of Eu provides the larger 25 nm grains for the Bi$_2$S$_3$: Eu (3%) thin film. The formation of a nanorod structure is confirmed by FESEM photos. High absorption and a low optical band gap (2.17 eV) were noticed for the 3% Eu doped sample. The conducted I-V test showed that the coated thin films exhibited admirable photocurrent conversion for the UV source. The Bi$_2$S$_3$ film with 3% Eu concentration displayed high performance with photoresponsivity, detectivity, and external quantum efficiency of 3.88 × 10$^{-1}$ AW$^{-1}$, 1.82 × 10$^{10}$ Jones, 125% at 5 V, respectively. The findings of the current study can be used in advanced functional optoelectronic applications.

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