p-type Cu₃BiS₃ thin films for solar cell absorber layer via one stage thermal evaporation

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Abstract

Ternary copper sulphides, especially copper-bismuth-sulphide (Cu-Bi-S), are alternative solar absorber materials due to their earth-abundant and non-toxic constituent elements, compared to the conventional copper indium gallium sulphide and cadmium telluride films. In this study, Cu-Bi-S thin films were deposited onto soda lime glass substrates using a one stage co-evaporation process from Cu₂S and Bi₂S₃ sources, with the deposition temperatures varied from room temperature to 400°C. X-ray diffraction analysis confirmed that Cu₃BiS₃ was the dominant phase in the Cu-rich films, and the crystalline quality of the films was significantly improved with increasing the deposition temperature. An optical bandgap of 1.4 eV was achieved for the film deposited at 400°C, which demonstrated a Hall mobility of 3.95 cm²/V-s and a carrier concentration of 7.48 × 10¹⁶ cm⁻³. Cu₃BiS₃ films deposited at 375 and 400°C were implemented into superstrate solar cell structures (glass/ITO/n-CdS/p-Cu₃BiS₃/Al).

Keywords: p-Cu₃BiS₃; thermal co-evaporation; absorber layer; thin film solar cell; optical band gap

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1. Introduction
Thin film materials, such as copper indium gallium sulphides (CIGS) and cadmium telluride (CdTe), have shown great potentials as photovoltaic absorbers with efficiency >22% demonstrated [1], and commercial production has been established [1-5]. However these thin film solar cell materials are comprising of either scarce, expensive and/or toxic elements, thus resulting in high manufacturing cost or unfriendly impact on the environment [1, 3]. It is essential to find an alternative thin film solar cell material with low-cost, non toxic and earth-abundant elements. Cu$_3$BiS$_3$, one of the copper bismuth sulphide (Cu-Bi-S) material system, is considered as a suitable alternate solar absorber material because of its promising photovoltaic properties along with its economical, abundant, and environment friendly constituent elements [6, 7]. Cu$_3$BiS$_3$, also known as the mineral wittichenite, was firstly synthesized in 1947 [8], but its potential as a solar absorber material was not recognized until 1997 [9]. Key photovoltaic properties of Cu$_3$BiS$_3$ include its inherently p-type conductivity [10], an optical band gap of ~1.4 eV close to the Shockley-Queisser optimum [11-14], and a strong optical absorption in the visible part of the spectrum [15, 16]. Mesa et al. [17] reported that the theoretical limit of the conversion efficiency of Cu$_3$BiS$_3$ is around ~19.86%. Despite these promising findings, investigations of the Cu$_3$BiS$_3$ for applications as solar absorber materials are rather limited [18-20]. Cu$_3$BiS$_3$ thin films with a p-type electrical conductivity of 0.03 (Ω.cm)$^{-1}$ were also prepared using a combined chemical and thermal process approach [15]. Moreover, the mobility of their photo-generated charge carriers was found to be $10^6$ cm$^2$/V s [15]. Li et al. developed a solution dip-coating route to synthesize phase-pure and highly crystalline Cu$_3$BiS$_3$ nanorods with lengths up to ~1.5-3 μm and widths of ~100-300 nm [21], and the photo-electric conversion (PEC) measurement of this material revealed its rapid responses to pulsed illumination and a promising photocurrents of ~1.0 x 10$^{-4}$ A/cm$^2$. Li et al. reported a Cu$_3$BiS$_3$ thin film solar cell of glass/Mo/Cu$_3$BiS$_3$/CdS/ZnO/ITO/Al using a dimethyl sulfoxide based solution coating process which showed an efficiency of 0.17% [22]. However in these solution processes, strong oxidization of the films causes significant recombinations of the photo-excited charge carriers, thus leading to poor performance of the solar cell device. Despite the great potential of this material as solar absorber material, until now there are few reports on the photovoltaic devices and optoelectronic characteriztion of Cu$_3$BiS$_3$ [31]. Furthermore, the best power conversion efficiency reported is only 1.28% [12, 23].

Cu$_3$BiS$_3$ thin films (with Wittichenite structures) have been extensively synthesized using both physical and chemical deposition techniques such as thermal evaporation [24, 25], sputter deposition [26], spin coating [27], electrodeposition [11], slovethermal deposition [28], spray
pyrolysis [29, 30] and chemical bath deposition [31]. Among these, thermal evaporation shows the potential for large-scale fabrication. In this paper, we will use a new method of co-evaporating Cu$_2$S and Bi$_2$S$_3$ precursors onto the soda lime glass substrates for the fabrication of Cu-Bi-S thin films, at different substrates temperatures ranging from room temperature to 400 °C. The films deposited at 375 and 400 °C were then implemented into thin film solar cells with a superstrate configuration (glass/ITO/n-CdS/p-Cu$_3$BiS$_3$/Al) and its performance were investigated.

2. Methodology

2.1 Deposition of thin films

The substrates used in this research work were soda-lime glass slides, acquired from Testbourne Ltd, UK. They were ultrasonically cleaned in a sequence using acetone, isopropanol (IPA) and deionized (DI) water, and then dried with nitrogen gas. The cleaned substrates were immediately placed into the deposition chamber before evacuating to $1 \times 10^{-6}$ mbar.

Anhydrous powder of copper(I) sulphide (Cu$_2$S) and bismuth sulphide (Bi$_2$S$_3$), of both 99% purity from Sigma-Aldrich, were used as the starting materials. Tungsten boats used for all the evaporation were acquired from Testbourne Ltd, UK. Each source was individually calibrated before co-evaporating Cu$_2$S and Bi$_2$S$_3$. A stable evaporation rate of 8 to 9 Å/s was obtained for the deposition of Cu$_2$S and Bi$_2$S$_3$ with the current values of 120 and 90 A, respectively, for the entire process until the estimated thickness of 2500 nm was obtained, which took ~29 min. The sources were shadowed with baffles in order to produce a composition gradient along the substrate and obtain Cu-Bi-S thin film libraries with a fix substrate position. The substrates were heated for the samples grown at different growth temperatures ranging from 275-400 °C.

2.2. Solar Cell Structure and Characterizations

The device with a superstrate configuration was fabricated using the Cu$_3$BiS$_3$ thin film as the solar absorber material. A CdS buffer layer was deposited using a chemical bath deposition (CBD) technique onto the glass coated with indium doped tin oxide (with a thickness of 60 nm) before the deposition of the absorber layer. The absorber layer of Cu$_3$BiS$_3$ with a thickness of 2500 nm was deposited onto ITO/CdS layers using a thermal co-evaporation technique as stated in the above section. Finally metallic contacts with a circular area of 3 mm$^2$ were
deposited on top of the device by evaporating >99.9% pure aluminum (Al) using electron beam evaporation technique to complete the device fabrication.

XRD analysis of the produced samples was carried out using a Siemens D5000 diffractometer in Bragg-Brentano geometry, with an X-ray Cu-Kα source with a wavelength of 1.54 Å. Raman spectra measurement was performed using a Renishaw inVia Raman spectrometer with an Ar laser excitation source (514.5 nm). Morphology and elemental composition of the obtained samples were investigated using a scanning electron microscope (SEM, TESCAN MIRA3), equipped with Oxford Instruments energy dispersive X-ray spectroscopy (EDS). Optical characterization was performed using a Shimadzu spectrophotometer (UV-2600). The valence states of the constituent elements of the Cu$_3$BiS$_3$ thin film deposited at 400°C were evaluated using a Thermo Scientific K-Alpha X-ray photoelectron spectrometer (XPS) with a monochromatic Al Kα X-ray source (1486.6 eV). Elemental depth profiling was carried out using a secondary ion mass spectroscope (SIMS) with a Hiden Analytical gas ion gun and quadrupole detector. A primary Ar$^+$ beam was used to scan over an area of 500 × 500 μm$^2$ with an impact energy of 4 keV and a beam current of 200 nA. In order to remove sidewall effects, a gating area of 10% was used. Photocurrent–voltage (I–V) measurements were performed using a Keithley 2400 series source meter under air mass 1.5 illumination (100 mW/cm$^2$) provided by an Abet Technologies Sun 2000 solar simulator.

3. Results and discussion

Compositional analysis of the room temperature-deposited copper-bismuth-sulphide thin film library is shown in Fig. 1. The readings were obtained at 10 different positions and the distance between two measurement positions was about 7.5 mm. Across the whole sample, the Cu composition is varied between 49% and 16% and that of Bi is from 4% to 29%. There is a minor variation in S composition (45 to 54 %). The estimated compositions of the Cu$_x$Bi$_y$S$_z$ films in the fabricated library are represented across the figures which can be further confirmed by XRD analysis. The EDS spectra of the identified phases are also presented in Figure S1 in the supporting material.
Fig. 1: Elemental composition of room temperature-fabricated Cu-Bi-S thin film library, evaluated from the EDS spectra with respect to distance across the sample surface.

The samples deposited at room temperature and 250°C do not show any crystalline phases. Figure 2 shows the XRD patterns of the Cu-Bi-S thin films deposited at 400°C. The changes in peak positions and intensities can be clearly seen from the XRD results with respect to the changes in the concentration of the content of Cu and Bi across the sample surface. Three distinct phases, e.g. Cu$_3$BiS$_3$ (PDF# 43-1479), Cu$_{3.21}$Bi$_{4.79}$S$_9$ (PDF# 73-1202) and Cu$_{1.77}$Bi$_{4.57}$S$_8$ (PDF# 89-1596) of the Cu-Bi-S ternary system were identified in various regions of the deposited area. The above results are in good agreements with those reported by Wang et al [32] and Sugaki et al. [33] for the Cu-Bi-S system prepared from low-temperature experiments. Wittichenite Cu$_3$BiS$_3$ was observed to be the dominant phase.
Fig. 2: (a) XRD patterns of the Cu-Bi-S thin films deposited at 400°C at positions 2, 6 and 10 as in Fig 1, with the corresponding standards of the respective observed phases of the ternary Cu-Bi-S material system.

XRD results of the samples in Cu-rich region deposited at various substrate temperatures ranging from room temperature to 400°C are presented in Fig. 3. A predominant orthorhombic Cu3BiS3 structure (PDF# 43-1479) is observed for all the temperatures in this region as shown in the Fig. 3.
Fig. 3: XRD patterns of the fabricated samples prepared at different substrate temperatures ranging from room temperature to 400°C of the Cu-rich region of the obtained samples with the reference powder pattern for Cu$_3$BiS$_3$ (PDF# 43-1479).

All the observed peaks for the samples deposited at different growth temperatures belong to Cu$_3$BiS$_3$ phase according to the reference (PDF# 43-1479), as shown in Fig. 3. The numbers and intensities of the identified peaks were observed to increase with increasing growth temperature, and the highest intensity peaks were recorded for the sample deposited at 400°C. The crystallite size of samples was estimated using the Scherrer’s equation based on the peaks corresponding to (1 3 1) reflection:

$$D = \frac{0.94 \lambda}{\beta \cos \theta}$$  \hspace{1cm} (1)

where D is the crystallite size, $\lambda$ is the wavelength of the x-rays source used, $\beta$ is the peak width at half maximum (FWHM) and $\theta$ is the diffraction Bragg’s angle.

The crystallite size (D) of the films was observed to increase (38.4 ± 0.1 to 44.2 ± 0.1 nm) with increasing deposition temperature from 350 to 400°C, which is in agreement with those reported in literature [12, 16, 20, 24, 25]. Variations in numbers and intensities of the peaks of
Cu$_{3.21}$Bi$_{4.79}$S$_9$ and Cu$_{1.77}$Bi$_{4.57}$S$_8$ films were also observed with increasing substrate temperature. The XRD patterns of these compositions in the prepared libraries are presented in Figures S2 and S3 (Supporting information). It is clear from the patterns that increasing growth temperature leads to better crystalline quality.

Raman spectra of the obtained Cu$_3$Bi$_3$ samples are shown in Fig. 4. The main Raman vibration modes were observed at 280 and 470 cm$^{-1}$ along with the low wave-numbers at 260 and 232 cm$^{-1}$ for the samples deposited at RT and 250°C. These are belonged to those of the wittichenite Cu$_3$BiS$_3$ phase of Cu-Bi-S ternary materials, based on the database RRUFF standard data [34] and literature [28, 35, 36]. The intensity of the dominant peak at 280 cm$^{-1}$ was observed to increase with increased deposition temperature indicating the improvement in the crystallinity of the fabricated samples. It is important to emphasis that no other modes for the binary or ternary compositions of Cu-Bi-S systems were observed in the Cu-rich region of the fabricated thin films, which is in line with that of the XRD analysis of these samples. The Raman spectroscopy and XRD analysis of the obtained samples provided us valuable information about the growth conditions to fabricate phase pure Cu$_3$BiS$_3$ without any other binary or ternary compounds of the Cu-Bi-S material system.

![Raman spectra plots](image)

**Fig. 4:** Raman spectroscopy plots of the fabricated Cu$_3$BiS$_3$ samples at different deposition temperatures ranging from room temperature to 400°C.
Figures 5 (a) to 5 (e) show the SEM images of the Cu$_3$BiS$_3$ thin film samples deposited at various substrate temperatures varying from room temperature (RT) to 400°C. Results showed that the morphologies of the obtained samples were significantly affected by the substrate deposition temperature.

**Fig. 5**: SEM images along with the EDS mapping of wittichenite Cu$_3$BiS$_3$ samples deposited on glass substrates at different substrate temperatures: (a) RT and at (b) 250°C (c) 350°C (d) 375°C (e) 400°C.

Figure 5 (a) shows that the surface of the film grown at RT consists of smooth microstructural features. However, with the increase of the substrate temperature to 250°C, agglomeration of structures occurs and an increase in the crystallite size can be observed from Fig. 5(b). Further increase of the substrate temperature up to 350°C results in rough surface features with some severely agglomerated particles as shown in Fig. 5 (c). When the substrate temperature is increased further to 375°C, significant agglomeration of structures occurs and correspondingly a non-uniform distribution of particles with some pinholes can be observed on the surface of the sample as shown in Fig. 5 (d). The shape of the surface particles turns into a columnar one with the increase in substrate temperature from 250 to 375°C, which might lead to a reduction
in recombination loss during PV process [37, 38]. Further increase of the substrate temperature to 400°C resulted in a smooth surface with large grains with few pinholes and voids as shown in Fig. 5 (e), indicating the improvement in the crystal growth of the samples with increasing substrate temperature. Insets of Fig. 5 shows the elemental mapping of the grown samples, which shows that there are no elemental aggregations for all the elements of the film, representing the smooth and uniform growth of the Cu₃BiS₃ thin film samples. Chemical states for the Cu₃BiS₃ thin film at position 2 deposited at 400°C on the glass substrate were obtained using the XPS anaylsis. The core level spectrum of Cu reveals a 2p doublet as shown in Fig. 6(a), at binding energies of 932.1 and 933.3 eV for Cu 2p₃/₂ and 952.1 and 952.9 eV for Cu 2p₁/₂, respectively, with a peak separation of 20.0 eV. The two Cu 2p doublet peaks show similar chemical shifts indicating the formation of a single compound of copper [39]. The dominant peaks at the binding energies of 932.1 and 952.1 eV are corresponding to Cu-Bi-S bonds while the lower intense peaks at binding energies of 933.3 and 952.9 eV are close to those of Cu-O bonds according to the XPS database [40]. The concentration of each peak to the main peaks from lower to higher binding energies are 56.8%, 20.6%, 15.9% and 6.5% respectively, with the peak areas (corrected using the relative sensitivity factors, RSF) of 3156.8, 1149.5, 888.7, and 361.0 as calculated from CasaXPS software. Accordingly, the ratio between the two peaks is estimated to be ~3:1.

The magnified core level spectrum of the bismuth 4f doublet state is shown in Fig. 6 (b). The peaks observed at 158.2 and 163.5 eV are related to Bi-S chemical bonds, which are the Bi 4f₇/₂ and 4f₅/₂ states with a peak separation of 5.3 eV. The component peaks at 159.0 and 164.3 eV are associated with Bi-O or Bi-O-S due to surface adsorption also with a peak separation of 5.3 eV. The Bi-O peak is very small, indicating its small quantities in the sample. The S 2p core level spectra with peak positions at 159.1, 160.7 and 162.0 eV are shown in Fig. 6 (c). The binding energies for S 2p are consistent with those in the sulphide phases [39, 41, 42]. The peak ratio of the Cu (2p), Bi (4f) and S (2p) bonds is ~ 3:1:3, indicating the formation of Cu₃BiS₃. These results agree with that of the XRD pattern of the synthesized thin film deposited at 400°C.
**Fig. 6**: High-resolution spectra of (a) Cu 2p core-level (b) Bi 4f core level and (c) S 2p core level of Cu₃BiS₃ thin film sample deposited at 400°C on a glass substrate. Black line is raw data, blue, pink and red lines are the deconvolved peaks.

In order to investigate the elemental distribution throughout the thickness of the synthesized films, Fig. 7 shows the depth profile for the Cu₃BiS₃ film deposited at 400°C on the glass
substrate using the SIMS. It can be noticed that the distribution of the elements along the thickness of the film is not uniform throughout the layer. The sharp change in the first 20 nm is due to surface oxidation and enhancement of ion yields upon sputtering. As can be seen from the plot, the surface up to ~500 nm of the sample is S-rich, however the distributions of all the three constituent elements become uniform when reaching to the substrate.

![Graph](image.png)

**Fig. 7**: SIMS depth profiles for a Cu$_3$BiS$_3$/glass film deposited at 400°C growth temperature.

Optical transmittance and reflectance properties of the Cu$_3$BiS$_3$ films deposited at different substrate temperatures are shown in Fig. 8 in the wavelength range of 300-1400 nm. The transmittance values are found to be from 4% to 55% in the wavelength range of 800-1400 nm. However, the transmittance in the visible region of the spectrum is lowest for all samples grown at various substrate temperatures, indicating the good absorption capability of the samples. The reflectance of the samples shown in the inset of Fig. 8 is decreased from ~ 40% to 4% in the visible wavelength region at 700 nm which is attributed to the enhancement of absorption with regularly arranged crystal orientations due to the increased substrate temperature.
Fig. 8: Optical analysis of the obtained wittichenite Cu$_3$BiS$_3$ samples grown at various substrate temperatures ranging from RT to 400°C on glass substrates, transmittance, inset figure shows reflectance.

The reflectance spectra of the samples grown at different substrate temperatures (250 and 350°C) is wavy-shaped in the entire wavelength range, revealing the non-homogenous distribution of the particles on the surface of these films and an indication of thickness interferences. The optical band gap energies of the films were further calculated using the standard Tauc’s relation [13, 14, 16],

\[(\alpha h\nu)^n = A (h\nu - E_g),\]  

(2)

where $E_g$ is the optical band gap energy, $\alpha$ is the absorption coefficient at a frequency of $\nu$, $A$ is constant and $n = 2$ and 1/2 for the allowed direct and indirect transitions, respectively. The optical absorption coefficient was calculated using the following relation:

\[\alpha = \frac{1}{d} \ln \left[ \frac{(1-R)^2}{T} \right]\]  

(2)
where $d$, $R$, and $T$ are the thickness, reflectance spectra and transmittance spectra of the fabricated Cu$_3$BiS$_3$ thin films, respectively.

![Optical characteristics](image)

**Fig. 9:** Optical characteristics (absorption coefficient) of the obtained wittichenite Cu$_3$BiS$_3$ samples grown at various substrate temperatures ranging from RT to 400°C on glass substrates, inset of the figure shows the Tauc plots for obtaining optical band gaps.

The optical absorption coefficient of the fabricated samples was found to be of the order of $\sim 10^5$ cm$^{-1}$ as shown in Fig. 9. The optical band gap of the sample deposited at room temperature was calculated from the Tauc plots and was found to be $\sim 2.0 \pm 0.1$ eV, while it was found to decrease to $1.4 \pm 0.1$ eV for the sample deposited at 400°C as displayed in the inset of Fig. 9. This is very close to the optimal band gap value (1.5 eV) for the solar absorber material. The optical bandgaps and absorption coefficients of Cu$_{3.21}$Bi$_{4.79}$S$_9$ and Cu$_{1.77}$Bi$_{4.57}$S$_8$ compositions of Cu-Bi-S material system were also obtained, and they are increased with increasing growth.
temperature as presented in the supporting materials (Fig. S4 and S5). Figure 10 shows the obtained optical bandgaps vs growth temperature of the obtained Cu$_3$BiS$_3$ samples grown at various substrate temperatures. Clearly there is a decreasing trend in the optical band gaps with respect to growth temperature.

![Graph showing band gap vs growth temperature](image)

**Fig. 10:** Optical band gap vs growth temperature of the obtained wittichenite Cu$_3$BiS$_3$ samples grown at various substrate temperatures ranging from RT to 400°C.

All the optical analysis data shows that the Cu$_3$BiS$_3$ films are suitable for the absorber layer in thin film solar cells. The bandgap values are similar with those reported in the literature [13, 28, 35, 36]. At a high deposition temperature, the grain growth and reduction in the impurities are responsible for the decrease in the band gap values [43].

The electrical properties of the Cu$_3$BiS$_3$ thin films were studied using the Hall-effect measurement, and the calculated values of the sheet resistance (R$_s$), Hall coefficient (R$_{H}$), Hall mobility ($\mu$) and carrier concentrations ($p$) are presented in Table 1. The Hall coefficient was observed with a positive sign indicating the p-type conductivity for the all samples deposited at different substrate temperatures ranging from RT to 400°C. The sheet resistance of the Cu$_3$BiS$_3$ thin films was found to decrease with increasing growth temperature as can be seen from Table 1, showing the improvement in the conductivity of the samples.
Table 1: Electrical characteristics of deposited Cu$_3$BiS$_3$ thin films on a glass substrate at different substrate temperature calculated using Hall Effect measurement.

<table>
<thead>
<tr>
<th>Sample (°C)</th>
<th>$R_s$ ($\Omega/\square$)</th>
<th>$R_{HS}$ (m$^2$/C)</th>
<th>$\mu$ (cm$^2$/V-s)</th>
<th>$\rho$ (cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT</td>
<td>$7.2 \times 10^3$</td>
<td>47.800</td>
<td>0.11</td>
<td>$1.300 \times 10^{13}$</td>
</tr>
<tr>
<td>250</td>
<td>6175</td>
<td>2.440</td>
<td>0.67</td>
<td>$2.550 \times 10^{14}$</td>
</tr>
<tr>
<td>350</td>
<td>2147</td>
<td>0.306</td>
<td>1.42</td>
<td>$2.040 \times 10^{15}$</td>
</tr>
<tr>
<td>375</td>
<td>95</td>
<td>0.001</td>
<td>2.05</td>
<td>$6.160 \times 10^{16}$</td>
</tr>
<tr>
<td>400</td>
<td>41</td>
<td>0.008</td>
<td>3.95</td>
<td>$7.480 \times 10^{16}$</td>
</tr>
</tbody>
</table>

The lowest sheet resistance ($41 \Omega/\square$) was observed for the sample deposited at 400°C (as listed in the Table 1). This results in an electrical conductivity of ~500 $\Omega$ cm$^{-1}$ for a film of 2500 nm thick. The highest values of the Hall mobility (3.95 cm$^2$/V-s) and carrier concentration ($7.480 \times 10^{16}$ cm$^{-3}$) were also observed for the sample deposited at 400°C.

Using the Cu$_3$BiS$_3$ samples deposited at 375 and 400°C as the absorber layer, solar cell devices were fabricated following the conventional superstrate configuration, i.e., glass/ITO/n-CdS/p-Cu$_3$BiS$_3$/Al as shown in the schematic diagram in the inset of Fig. 11.
Figure 11: Photovoltaic characteristic of the grown wittichenite Cu$_3$BiS$_3$ thin film solar cells at 375 and 400°C a typical I-V curves of the obtained device under illumination of 100 mW/cm$^2$, insets are the schematic diagram and the cross sectional SEM image of the device.

A cross-sectional SEM image of the solar cell device is also presented in the inset of Fig. 11, which shows no clear separation among the layers of the obtained device, indicating good adhesion with the ITO substrate and different layers. The fabricated devices were tested for the current-voltage (I-V) characteristic in both dark and illumination conditions, and the results are shown in Fig. 11. The Cu$_3$BiS$_3$ thin film solar cell devices grown at 375 and 400°C showed a definite photovoltaic behaviour and the photocurrent was observed to increase from 1.0 to 3.0 mA under illumination at 0.9 V, as shown in Fig. 11.

Although the device performance is still poor, the definite photovoltaic behavior exhibited by our initial device directly evidences the potential applications of Cu$_3$BiS$_3$ in solar cells. The poor collection of the photogenerated carriers implied to quite low photocurrent which is probably mainly limited by the imperfect junction formation between Cu$_3$BiS$_3$ and CdS layers, which might be due to the deposition process. Another possible cause is the improper band gap
alignment between CdS and Cu$_3$BiS$_3$ layers [20, 24, 36]. Further in-depth work is essentially required to confirm the spike-like conduction band offset at the interface, which might be beneficial to reduce the carrier recombination. Furthermore, interdiffusion is another key issue that commonly influences the interface behavior in chalcogenide solar cells [12, 20], which needs to be further explored.

4. Conclusion

Thin films of Cu-Bi-S material system were fabricated at various deposition temperatures ranging from room temperature to 400°C. From the structural analysis of Cu-Bi-S thin film samples, wittichenite Cu$_3$BiS$_3$ phase was confirmed to be the dominant phase in the Cu-rich region of the samples at all deposition temperatures and the crystalline quality of all the fabricated samples was increased with increasing substrate temperature from RT to 400°C. The optical band gap of 1.4 ± 0.1 eV, good electrical conductivity of ~ (500 Ω$^{-1}$cm$^{-1}$), mobility ~ (3.95 cm$^2$/V-s) and carrier concentration ~ (7.48 × 10$^{16}$ cm$^{-3}$) for Cu$_3$BiS$_3$ grown at 400°C highlighted the suitability of this composition for the solar cell absorber layer. Finally, the Cu$_3$BiS$_3$ films grown at 375 and 400°C was implemented into thin film solar cell structure in the superstrate configuration and increase (1.0-3.0 mA) in the photocurrent was observed under illumination at 0.9 V.

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