Enhanced Electrical Conductivity of Sb$_2$S$_3$ Thin Film via C$_{60}$ Modification and Improvement in Solar Cell Efficiency

Chunsheng Guo, Jingwei Chen, Gang Li, Xiaoyang Liang, Weidong Lai,*
Lin Yang, Yaohua Mai, and Zhiqiang Li*

Sb$_2$S$_3$ has attracted great research interest very recently as a promising absorber material for photoelectric and photovoltaic devices because of its unique optical and electrical properties and single, stable phase. However, the intrinsic high resistivity property of Sb$_2$S$_3$ material is one of the major factors restricting the further improvement of its application. In this work, the C$_{60}$ modification of Sb$_2$S$_3$ thin films is investigated. The conductivity of Sb$_2$S$_3$ thin films increases from $4.71 \times 10^{-6}$ S cm$^{-1}$ for unmodified condition to $2.86 \times 10^{-8}$ S cm$^{-1}$ for modified thin films. Thin-film solar cells in the configuration of glass/(SnO$_2$:F) FTO/TiO$_2$/Sb$_2$S$_3$(C$_{60}$/Spiro-OMeTAD)/Au are fabricated, and the conversion efficiency is increased from 1.10% to 1.74%.

1. Introduction

In recent years, a great deal of effort has been devoted to explore the application of novel materials such as Cu$_2$ZnSn(S,Se)$_4$,[1,2] SnS,[1] CuSb(S,Se)$_2$,[4,5] GeSe,[6] Sb$_2$(S,Se)$_3$[7–11] for light absorption materials for solar energy conversion. Among them, antimony sulfide (Sb$_2$S$_3$) is a binary semiconductor compound with a single stable phase, which could avoid the formation of other secondary phases.[12] In particular, Sb$_2$S$_3$ received considerable attention for light absorber material in solar cells due to its suitable bandgap of 1.7–1.8 eV with high absorption coefficient of $10^5$ cm$^{-1}$ in the visible range, abundant and environmental friendly compositional elements, and excellent air stability.[13–15] This bandgap allows its application as absorber in single-junction solar cell or in top cell of the multijunction tandem photovoltaic device.

Sb$_2$S$_3$ has been studied as an absorber material for photovoltaic devices with a conversion efficiency as high as 7.5% in 2014, by post-treatment for reducing the trap sites in Sb$_2$S$_3$.[16]

On the other hand, Sb$_2$S$_3$-based planar heterojunction solar cells also gained great progress in device fabrication, device structure improvement, and so on. Compared to the several nanometers-thick absorber in Sb$_2$S$_3$-sensitized solar cells, the thickness of Sb$_2$S$_3$ absorber in planar heterojunction solar cell was in scale of hundreds of nanometers. Both the surface defect and bulk defect played critical roles in dictating solar cell device performance. The intrinsic high resistivity property of Sb$_2$S$_3$ material was one of the major factors restricting the further improvement of device performance.[18] Introducing other elements as dopant to modify the host system or forming ternary alloyed compounds was an efficient route to tailor the electronic band dispersion, adjust the carrier concentration, or even vary the conductivity type of the Sb$_2$S$_3$-based semiconductor. Very recently, Tang et al. reported controllable sulfur vacancy defect by introducing Zn ion into the films. The behavior of electron concentration in Sb$_2$S$_3$ layer was observed to increase with sulfur vacancy defects, which resulted in reduced series resistance and increased recombination resistance for the Sb$_2$S$_3$ thin film solar cells.[19]

The carrier diffusion length of Sb$_2$S$_3$ could reach hundreds of nanometers,[14] which allowed its application in both sensitized mesoporous device structure and planar heterojunction solar cell configuration. Sb$_2$S$_3$ was employed as semiconductor sensitizer in mesoscopic solar cells in 2009, where the extremely thin Sb$_2$S$_3$ absorber (between several nanometers and several tens of nanometers) was made using chemical bath deposition (CBD), and a conversion efficiency of 3.37% was obtained.[16] Choi et al. reported conversion efficiency as high as 7.5% in 2014, by post-treatment for reducing the trap sites in Sb$_2$S$_3$.[17]

C. Guo, Dr. J. Chen, G. Li, X. Liang, Dr. W. Lai, Dr. L. Yang, Y. Mai, Dr. Z. Li
Hebei Key Laboratory of Optic-Electronic Information and Materials
College of Physics Science and Technology
Hebei University
Baoding 071002, China
E-mail: laiwd@hbu.edu; lizhiqiang@hbu.edu.cn
Prof. Y. Mai
Institute of New Energy Technology
Jinan University
Guangzhou 510632, China

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/gch2.201800108.
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for post-treated thin films, while the bandgap for carbon-doped sample was kept nearly values with the undoped crystalline Sb\textsubscript{2}S\textsubscript{3} thin films.\textsuperscript{[18]} The investigation of the carbon doping on Sb\textsubscript{2}S\textsubscript{3} was not enough.

In this work, we explore the C\textsubscript{60}-modified Sb\textsubscript{2}S\textsubscript{3} thin films by spin coating. The presence of C\textsubscript{60} was checked by scanning electron microscopy (SEM) and Raman spectra. Both of the longitudinal and transverse conductivity of the Sb\textsubscript{2}S\textsubscript{3} layer with and without C\textsubscript{60} modification was analyzed. Planar solar cells in configuration of glass/SnO\textsubscript{2}:F (FTO)/TiO\textsubscript{2}/Sb\textsubscript{2}S\textsubscript{3}(C\textsubscript{60})/Spiro:OMeTAD/Au were fabricated. The solar cells employing C\textsubscript{60}-modified Sb\textsubscript{2}S\textsubscript{3} absorber show better short-circuit current, fill factor (FF), and conversion efficiency. Furthermore, the physical mechanism behind this improvement was discussed.

2. Results and Discussion

The surface morphologies of Sb\textsubscript{2}S\textsubscript{3} thin films with and without C\textsubscript{60} modification were characterized by SEM. As shown in Figure 1, the Sb\textsubscript{2}S\textsubscript{3} layer was smooth and uniform without any pinhole or particle agglomeration that could be observed, which was in agreement with the previous reports. A large number of small bright dots were observed from the SEM image of the C\textsubscript{60}-modified Sb\textsubscript{2}S\textsubscript{3} thin films. In order to characterize the small bright spots on the film that were caused by C\textsubscript{60} modification, we carried out the Raman spectra measurement in the wavenumber range of 150–600 and 1300–1700 cm\textsuperscript{-1}, respectively. As show in Figure 2a, in the range between 150 and 600 cm\textsuperscript{-1}, both of the Raman spectra exhibited similar behaviors, and four peaks at 188, 237, 280, and 303 cm\textsuperscript{-1} could be observed. The peaks centered at 188, 237, 280, and 303 cm\textsuperscript{-1} correspond to the vibration of the Sb−Sb bond for Sb\textsubscript{2}S\textsubscript{3} structural units, to the antisymmetric S−Sb−S vibration, the antisymmetric vibrations of Sb−S stretching in pyramidal symmetry, and the symmetric stretching of the Sb−S structural units, respectively.\textsuperscript{[21]} On the contrary, the Raman spectra in the range of 1300–1700 cm\textsuperscript{-1} displayed very different behaviors (Figure 2b). The Raman spectrum of bare Sb\textsubscript{2}S\textsubscript{3} sample was smooth and no obvious peaks could be observed, while that of C\textsubscript{60}-modified sample showed peaks at 1609, 1668, 1565, and 1434 cm\textsuperscript{-1}, respectively. The peak centered at 1609 and 1668 cm\textsuperscript{-1} was corresponding to the vibration of H\textsubscript{g} symmetry in the C\textsubscript{60} unit.\textsuperscript{[22,23]} The peaks centered at 1434 and 1565 cm\textsuperscript{-1} could be indexed to the A\textsubscript{g} and H\textsubscript{g} vibration mode of C\textsubscript{60}.\textsuperscript{[24]} This result suggested the presence of C\textsubscript{60} in the Sb\textsubscript{2}S\textsubscript{3} films. It should be noted that the X-ray diffraction (XRD) patterns of bare and C\textsubscript{60}-modified Sb\textsubscript{2}S\textsubscript{3} thin films showed nearly the same behavior with each other. As shown in Figure 2c, both the XRD patterns of the bare and C\textsubscript{60}-modified Sb\textsubscript{2}S\textsubscript{3} films could be indexed to the orthorhombic structure of Sb\textsubscript{2}S\textsubscript{3} (JCPDS: 06-0474), and no other impurity phase or any shift could be observed. This behavior was much different from the case of metal or non-metal element doping in the Sb\textsubscript{2}S\textsubscript{3} thin films.\textsuperscript{[19,25]} The lattice parameters a, b, and c of the bare Sb\textsubscript{2}S\textsubscript{3} film were calculated to be 4.722, 5.695, and 15.681 Å, respectively. On the contrary, the parameters for the C\textsubscript{60}-modified Sb\textsubscript{2}S\textsubscript{3} film were 4.725, 5.691, and 15.673 Å, respectively. In addition, the transmittance spectra of the C\textsubscript{60}-modified Sb\textsubscript{2}S\textsubscript{3} film was basically the same as that of bare Sb\textsubscript{2}S\textsubscript{3} film (Figure 2d). These results hinted that the presence of C\textsubscript{60} did not induce any lattice distortions for Sb\textsubscript{2}S\textsubscript{3} thin films. In addition, the optical bandgap of the unmodified Sb\textsubscript{2}S\textsubscript{3} and C\textsubscript{60}-modified Sb\textsubscript{2}S\textsubscript{3} films was calculated to be about 1.76 eV, obtained from the optical transmittance spectra, which was very close to the values obtained by external quantum efficiency (EQE) curves (Figure 3b).

We further characterized the effect of C\textsubscript{60} modification on the photoconductivity of Sb\textsubscript{2}S\textsubscript{3} thin film. Both the transverse and longitudinal optical flow responses of the bare and C\textsubscript{60}-modified Sb\textsubscript{2}S\textsubscript{3} thin films were measured in a certain time domain (Figure 4). In the case of transverse photocurrent response measurement, a Sb\textsubscript{2}S\textsubscript{3} film with or without C\textsubscript{60} was spin-coated directly onto the FTO glass substrate as the photon-absorber layer, followed by the thermal evaporation of a 50 nm thick gold electrode on the Sb\textsubscript{2}S\textsubscript{3} film. The device structure of glass/Sb\textsubscript{2}S\textsubscript{3}(C\textsubscript{60})/Au is formed as shown in Figure 4a.\textsuperscript{[26]} Figure 4b exhibited the light and dark transverse photocurrent responses of the bare and C\textsubscript{60}-modified Sb\textsubscript{2}S\textsubscript{3} thin films as functions of time, where the photo current was generated with irradiation of a white LED with a power density of 5 mW cm\textsuperscript{-2}. The photocurrent of the bare and C\textsubscript{60}-modified Sb\textsubscript{2}S\textsubscript{3} thin films exhibited good repeatability. The photocurrent and dark current of bare Sb\textsubscript{2}S\textsubscript{3} thin film was 4.53 × 10\textsuperscript{-5} and 3.18 × 10\textsuperscript{-6} mA, respectively. The transverse electrical conductivity of the bare Sb\textsubscript{2}S\textsubscript{3} thin film was low (4.71 × 10\textsuperscript{-9} and 3.43 × 10\textsuperscript{-10} S cm\textsuperscript{-1}) and consistent with the values in previous references. In addition, the C\textsubscript{60}-modified Sb\textsubscript{2}S\textsubscript{3} thin film and bare Sb\textsubscript{2}S\textsubscript{3} thin film were subjected to current density–voltage (J–V) test under light illumination, as shown in Figure 4c. However, the C\textsubscript{60}-modified Sb\textsubscript{2}S\textsubscript{3} thin film showed...
higher conductivity (2.86 × 10⁻⁸ and 2.24 × 10⁻⁸ S cm⁻¹) both under light illumination and dark conditions. This was also confirmed by the J–V curves in Figure 4c.

For longitudinal photoconductivity measurement, we fabricated the Sb₂S₃-based devices in configuration of glass/FTO/TiO₂/Sb₂S₃(C₆₀)/Spiro-OMeTAD/Au. In the device shown...
in Figure 4d, the light passed through glass, FTO, and TiO$_2$ layer, and was absorbed in the Sb$_2$S$_3$ layer, resulting in the generation of carriers. The photon-generated carriers were extracted by TiO$_2$ and Spiro-OMeTAD layers and collected by FTO and gold contact. Figure 4e displays the longitudinal photocurrent responses of the device with bare or C$_{60}$-modified Sb$_2$S$_3$ films as a function of time. It was observed that both samples exhibited good repeatability and stability as the transverse photocurrent response spectra. Both dark currents were low but the photocurrent was much different. The photocurrent of the bare Sb$_2$S$_3$ sample was around 40 $\mu$A, while that of the C$_{60}$-modified Sb$_2$S$_3$ sample was higher than 70 $\mu$A under light condition. This result suggested that both the transverse and longitudinal photoconductivity of the Sb$_2$S$_3$ thin films could be improved by C$_{60}$ modification.[26,27]

The photovoltaic characteristics of the solar cells, in superstrate configuration, with bare Sb$_2$S$_3$ and C$_{60}$-modified Sb$_2$S$_3$ absorber layers, respectively, were measured under AM 1.5G illumination. The $J$–$V$ curves of the devices are shown in Figure 3a. The solar cell with bare Sb$_2$S$_3$ absorber exhibited an open-circuit voltage ($V_{OC}$) of 0.465 V, short current density ($J_{SC}$) of 7.03 mA cm$^{-2}$, FF of 33.54%, and a power conversion of 1.10%, respectively. The cell with C$_{60}$-modified Sb$_2$S$_3$ absorber showed a power conversion of 1.75% with a $V_{OC}$ of 0.492 V, $J_{SC}$ of 8.44 mA cm$^{-2}$, and FF of 42.15%. As shown in Figure 3b, the edge of EQE spectra of the Sb$_2$S$_3$ and C$_{60}$-modified Sb$_2$S$_3$ solar cells were about 750 nm, but the plateau region was different from each other. The EQE spectra of the Sb$_2$S$_3$ solar cells sharply decreased at about 400 nm, which could be ascribed to the incomplete collection of photogenerated carriers in the solar cell. In the contrast, the plateau region of EQE for C$_{60}$-modified Sb$_2$S$_3$ solar cells was beyond 400 nm, indicating that the presence of C$_{60}$ can effectively enhance the collection length of photogenerated carriers in the device. Furthermore, the biased EQE measurement in Figure 3c exhibited higher EQE values under $-0.2$ V bias voltage, suggesting an enhanced carrier collection.[28,29]

To further explore the charge transport characteristics of the device, we performed the electrochemical impedance spectroscopy (EIS) measurement. The impedance spectra of the devices were recorded at a potential of 0 V at frequencies ranging from 1 Hz to 0.1 MHz. The Nyquist plots are shown in Figure 5, and the inset is the equivalent electrical circuit model for the Sb$_2$S$_3$-based thin film solar cell. The equivalent circuit diagram consisted of a series connection of a resistor (R$_1$), a parallel combination of a constant phase element (CPE1), and a resistor (R$_2$).[30–32] In this experiment, the resistor R$_1$ was related to the internal series resistance of the device, and R$_2$ was the starting point of the real part in the Nyquist plots. R$_1$ and CPE1 were associated with the interface of the absorber layer and the TiO$_2$ layer. CPE1 can be represented by a capacitor (CPE1-T) and a nonhomogeneity constant (CPE1-P). The fitting results for these parameters are shown in Table 1. The value of R$_1$ for the solar cell with bare Sb$_2$S$_3$ absorber was 33.23 $\Omega$ cm$^2$, while that for the device with C$_{60}$-modified Sb$_2$S$_3$ absorber decreased to 9.22 $\Omega$ cm$^2$. Moreover, the values for the composite resistors R$_2$ were raised from untreated 1358 to 23680 $\Omega$ cm$^2$ after modification. The results indicated that the modification of C$_{60}$ on Sb$_2$S$_3$ facilitated charge transport from absorber to the TiO$_2$ layer with less recombination.[33–35]
3. Conclusion

In summary, the addition of C₆₀ into the solution-processed Sb₂S₃ thin films enhanced the transverse and longitudinal conductivity of the Sb₂S₃ films. The crystallinity and optical properties exhibited nearly the same behavior for the Sb₂S₃ films with and without C₆₀ modification. The presence of C₆₀ can effectively improve the thin film conductivity and facilitate the collection of photogenerated carriers in the absorber layer. Thus, the Sb₂S₃-based planar heterojunction solar cells exhibited higher conversion efficiency after C₆₀ modification. EIS measurement showed that the C₆₀-modified Sb₂S₃ thin film solar cell had a smaller series resistance and less interface recombination.

4. Experimental Section

The Sb₂S₃ thin film was deposited by spin coating on a commercial FTO glass substrate covered with a 50 nm thick TiO₂ layer. The TiO₂ layer was deposited by spin coating at 5000 rpm for 30 s and annealing in a muffle furnace at 500 °C for 60 min. The Sb₂S₃ precursor solution was prepared as follows: 1.0 mmol of Sb₂O₃ powder was dissolved in a mixed solution of 2.0 mL of anhydrous ethanol (CH₂CH₂OH, AR) and 1.5 mL of carbon disulfide (CS₂), and then 2.0 mL of n-butylamine (CH₃(CH₂)₃NH₂, GR 99.5%) was slowly added to the vial and stirred at room temperature. After stirring well, 2.16 mL of C₆₀ solution was added to 1 mL of Sb₂S₃ precursor solution and stirred. Three hundred nanometers of Sb₂S₃ layers with and without C₆₀ modification were deposited on commercial FTO glass, coated with a TiO₂ layer, by spin coating at 3000 rpm for 60 s. Following the deposition, thin film was annealed on a hot plate in N₂-purge glove box at 100 °C for 1 min and 300 °C for 2 min. Sixty nanometers of Spiro-OMeTAD was spin-coated on Sb₂S₃ (C₆₀)/TiO₂/FTO substrate for 30 s at 3000 rpm as the hole transport layer. Solar cells were manufactured using the glass/FTO/TiO₂/Sb₂S₃ (C₆₀)/Spiro-OMeTAD/Au structure. Gold contacts of 70 nm thickness and 0.09 cm² area were deposited by thermal evaporation.

The surface morphology of bare and C₆₀-modified Sb₂S₃ thin films was characterized by SEM (FEI nova nano SEM450). XRD patterns of the films were characterized by XRD with Cu Kα (1.54056 Å) radiation (Bruker D8 Advance), and the optical properties of the films were measured using a spectrophotometer equipped with an integrating sphere (Perkin-Elmer Lambda 950). In order to characterize the presence of C₆₀ in the C₆₀-modified film, Raman measurements were performed using Raman spectrometer (Horiba Jobin Yvon, HR Evolution) equipped with the 532 nm line of the laser. Under standard test conditions (25 °C, AM 1.5, 100 mW cm⁻²), the J–V measurements were performed on bare and C₆₀-modified Sb₂S₃ thin film solar cells using an AM 1.5 solar simulator equipped with a 300 W xenon lamp (Model No. XES-10051, SAN-EI, Japan). EQE of the bare and C₆₀-modified Sb₂S₃ film was obtained by Enlitech QER3011 system. Carrier transporting behavior of the device was characterized by EIS (PP211, ZAHNER, Germany) under appropriate open-circuit voltage.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

antimony sulfide, C₆₀ modification, lattice distortion, photodetectors, solar cells, thin films

Table 1. Fitted parameters of the equivalent circuit from the EIS measurements.

| Absorber     | Rₛ [Ω cm²] | CPE1-T [10⁻⁴ F cm⁻²] | CPE1-P [F cm⁻²] | Rₒ [Ω cm²] |
|--------------|------------|-----------------------|-----------------|------------|
| Sb₂S₃        | 33.23      | 7.13                  | 0.85            | 1358       |
| Sb₂S₃-C₆₀    | 9.22       | 6.49                  | 0.94            | 23680      |

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