Sb_2S_3 nanostructured composite materials for photovoltaics

Zhou Boyang

Graduate School of Energy Science

2022

Photovoltaic power generation is an effective means to convert sunlight into electrical energy, in which solar cells are the basic unit of photoelectric conversion, and the production cost and photoelectric conversion efficiency are directly related to the commercial application of photovoltaic devices. Currently, power conversion efficiency (PCE) of silicon based, cadmium telluride (CdTe), copper indium gallium selenide (CIGS), and perovskite solar cells have all been reported to have exceed 20%.[1] Due to the problems of toxicity, high cost, and stability of thin-film solar cells such as CdTe, CIGS, and perovskite, their application in production and life is also limited, and the market share is low, and they cannot replace silicon cells. Therefore, explore new materials, new structures, and new methods of solar cells, and develop tandem cells complementary to silicon cells is a must to improve device efficiency and reduce costs, thereby promoting the development of the photovoltaic industry.

Sb_2S_3 is a V-VI group compound semiconductor, and its crystal structure belongs to the orthorhombic Pnma 62 space group. Sb_2S_3 crystals are formed by infinitely extending $(Sb_4S_6)_n$ one-dimensional molecular chains and stacking to each other by van der Waals forces.[2, 3] Therefore, the crystal of Sb_2S_3 exhibits strong anisotropy, and Sb_2S_3 crystals tend to grow along the c-axis, and it is easy to obtain one-dimensional nanowire-like crystals. Sb_2S_3 is a simple binary inorganic compound with a single phase. It exists in the form of stibnite in nature. The characteristics of its low toxicity, low cost, stability, and facile preparation show great application prospects for Sb_2S_3 materials.[2]

According to literature reports and related theoretical calculations, the band gap of the polycrystalline Sb_2S_3 film is 1.73 eV, and the band gap of the amorphous film will increase to 2.2 eV.[1, 2] The efficiency of single junction Sb_2S_3 solar cell based on

Shockley-Queisser (S-Q) theoretical calculation can exceed 27%.[2] The absorption spectrum of the Sb_2S_3 film is in the range of 300-750 nm. Its absorption coefficient is 10^4-10^5 cm^{-1}, and it reaches 1.8×10^5 cm^{-1} in the range of 400-500 nm.[4] The reported carrier mobility of Sb_2S_3 films is in the range of 1-10 cm^2 $V^{-1}s^{-1}$ and the carrier concentration is 1.2×10^{12} cm^{-3}. [5] Due to the small carrier concentration of Sb_2S_3 thin film, it is a partial intrinsic semiconductor, and electron and hole transport layers are usually added in photovoltaic devices. Due to the strong anisotropy of Sb_2S_3, the electronic structure in the crystal is quite complex, and there is a huge difference in the intra-chain and inter-chain carrier transport properties. Therefore, the preparation of vertically oriented thin films is beneficial to obtain high-performance thin-film solar cells.

The development of planar junction Sb_2S_3 solar cells can date back to 1993, Savadogo and Mandal first use chemical bath deposition (CBD) method to fabricate n-Sb_2S_3/p-Si heterojunction solar cells with a 5.19% device efficiency.[6] In 2010, Darwish *et al*. directly prepared Sb_2S_3 thin films on the (100) surface of Si by thermal evaporation technology to obtain p-Sb_2S_3/n-Si solar cells with a conversion efficiency of 4.65%.[7] In 2014, Nair *et al*. introduced CdS into Sb_2S_3 cells as ETL, and the device achieved efficiency of 1.27%.[8] In 2016, Fang group adopted SnO_2 as ETL, and the efficiency of the device reaches 2.8%.[9] Commonly used n-type materials such as TiO_2, ZnO, CdS, SnO_2 can be matched with Sb_2S_3 to form a heterojunction. Among them, TiO_2 has the characteristics of stability and easy preparation, and is the most widely used material. In 2014, Kim *et al*. used atomic layer deposition (ALD) to prepare high-quality Sb_2S_3 thin films with a thickness of only 90 nm. The cell structure was FTO/c-TiO_2/Sb_2S_3/P3HT/Au, and the conversion efficiency reached 5.77%. As a comparison, the efficiency of Sb_2S_3 cells prepared by chemical bath deposition method is only 2.17%.[10] In 2015, Zimmermann *et al*. used the CBD method to prepare a cell with a structure of ITO/TiO_2/Sb_2S_3/P3HT/Ag, and optimized the thickness of the P3HT, obtaining a 4.06% conversion efficiency. The open circuit voltage was up to 0.726 V.[11] In the same year, Myoung Sang You *et al*. prepared Sb_2S_3 thin-film solar cell by spin coating method after preparing Sb and S precursor solutions, and achieved an efficiency of 2.3%.[12] The Zapien group fabricated ultrathin Sb_2S_3 thin-film cell by thermal evaporation method with a conversion efficiency of 1.94%.[13] Ma *et al*. used the solution method and prepared the solar cell with structure of ITO/TiO_2/Sb_2S_3/P3HT:PCBM/PEDOT:PSS/Ag with a conversion efficiency of 3.52%.[14] Mai *et al*. fabricated Sb_2S_3 thin film with the method of vapid thermal deposition and discovered the effect of crystallinity and preferred crystal growth on orientation on efficiency, and finally achieved 3.01% efficiency.[15] Lan *et al*. compared the film formation result by evaporating Sb_2S_3 and Sb_2S_5 powders, and proved that the device filling factor was better by using Sb_2S_5 as the evaporation source, and the device efficiency was 3.75%.[16] Chen Tao's research group has made great progress in the research of Sb_2S_3 planar junction cells. They developed and optimized the solution method to prepare Sb_2S_3.[17, 18] Also they explored the influence of inorganic hole transport layer (NiO_x [19] and V_2O_5 [20]) and absorption layer doping[21] on device efficiency. The efficiency increased from 4.3% to 6.56% after optimization. The cell efficiency prepared by co-evaporating Sb_2S_3 and S source also achieved 5.8%.[22] They also used the vacuum-assisted solution method to deposit Sb_2S_3 on TiO_2 nanorods, and the cell efficiency of this nanostructure reached 6.78%.[23] In 2021, Chen's group introduced a nucleation-annealing cycle method and successfully fabricated epitaxial grown Sb_2S_3 nanorod arrays on substrate, and thus prepared solar cell achieved an efficiency of 5.70%.[24] Due to the one-dimensional crystal structure, nanorods arrays is more favored for carrier directional transport between layers than bulk thin film. In this context, effective approaches to enhance the carrier mobility by applying Sb_2S_3 or Sb_2Se_3 nanorod arrays as light absorber are urgently required.

In this thesis, efforts have been made to synthesize Sb_2S_3 nanorods with high aspect ratio. A facile method of growing highly oriented Sb_2S_3 nanorod arrays on method was also introduced. Such prepared antimony chalcogenide nanorod array was used as light absorber and solar cells were fabricated. Further Sb_2Se_3 nanorod array was inherited on dense Sb_2S_3 nanorod array to fabricate heterojunction structure as light absorber, and the light-harvesting and charge extraction of such prepared solar cell was enhanced. Ternary $Sb_2(S_xSe_{1-x})_3$ nanorod array was also prepared by doping Se element into Sb_2S_3 nanorods.

Lastly, a hierarchical composite of Sb_2S_3 nanorods (NR) decorated on ZnO nanofibers (NF) scaffold structure was invented to discover possibilities of new structure of Sb_2S_3 based solar cell.

Initially, efforts have been made to synthesize Sb_2S_3 nanorod with high aspect ratio and high crystallinity. Three commonly used sulfur compounds were tried as precursor and three different types of Sb_2S_3 nanocrystal were prepared. Highly oriented Sb_2S_3 nanorod arrays were grown on a seed layer coated substrate. The optical and photoelectrical properties of these samples using different types of Sb_2S_3 nanorod arrays were characterized and compared with planar bulk sample, and the nanorod arrays prepared by using xanthate as precursor shows good crystallinity and carrier mobility.

The fabricated complete cell using the as prepared Sb_2S_3 nanorod arrays as light absorber was optimized. The sample of which the nanorod arrays prepared using xanthate as precursor exhibited the best performance for its best crystallinity and highest carrier mobility. Polyvinylpyrrolidone (PVP) was used as additive to make shorter and denser nanorod array layer, and so as to enhance the PCE of solar cell. The CBD time, hydrothermal reaction time and the precursor concentration were optimized to find the best nanorod array fabricating condition for solar cell. The solar cell using Sb_2S_3 with the length of ca. 300 nm as absorbing layer attained the highest PCE of 1.46% with a hole mobility of 30.9 $cm^2\ V^{-1}\ s^{-1}$. The device was also compared with randomly stack nanorods to show its superiority in carrier mobility and external quantum efficiency.

Also, ternary compound of antimony sulfide selenide was fabricated by a spin-coating and annealing method using the ethylenediamine solution of selenium. The band structure can be tuned by changing the concentration of the selenium solution used. The depth profiling suggested that the concentration of selenide basically did not change according to the depth in the nanorod array layer. The sample prepared by 10 mg ml^{-1} selenium solution exhibited the highest selenide concentration and achieved best PCE of 1.89%. The increased short circuit current density and decreased series resistance may be caused by the increased in carrier density when selenide was added.

Besides, a facile growth method of Sb_2Se_3 nanorod array grown on the glass-FTO based substrate loaded with Sb_2S_3 as seed layer by a simple and effective solvothermal method using $Sb(L)_2Cl_3$ (L= *N*,*N*-dimethyl selenourea) as single precursor was introduced. Different dispersion media and working conditions were optimized to get the appropriate products for the application of them as light absorbing layer for solar cells. The as prepared Sb_2Se_3 nanorod array were indexed to the orthorhombic phase of Sb_2Se_3. Based on the facts that the lattice coefficient and the crystal structure of Sb_2S_3 and Sb_2Se_3 are very similar to each other, the combination of Sb_2S_3 and Sb_2Se_3 for application of it as light absorbing layer for photovoltaic devices has been studied. Sb_2S_3 nanorod array/Sb_2Se_3 nanorod array heterojunction structure was prepared and was optimized by tuning the thickness of dense Sb_2S_3 nanorod array layer. Complete solar cells using such dense Sb_2S_3 nanorod array/Sb_2Se_3 nanorod array heterojunction as light absorbing layer was designed and attained a PCE of 1.50%. Compared with planar Sb_2S_3/planar Sb_2Se_3 heterojunction device, the nanoarray heterojunction revealed advantages in less defects and better carrier transport between the interfaces of heterojunction. This method of combining two layers of nanorod array together to prepare a heterojunction structure will enlighten more strategies of optimization of antimony chalcogenide active layer for photovoltaic devices.

Lastly, a preparation method for ZnO NF with Sb_2S_3 NR composite hierarchical structure by decorating Sb_2S_3 NR on ZnO NF through hydrothermal reaction was introduced. The morphology of Sb_2S_3 NR grown on ZnO NF hierarchical structure was controlled by changing the PVP concentration of the precursor solution. The NR size and growth preferred orientation can also be controlled by changing the PVP concentration. The mechanism of altering the morphology by changing the use amount of PVP was illustrated. The optical and electrical properties of Sb_2S_3 NR grown on ZnO NF hierarchical structure were also characterized. Complete cell with a structure of glass-(FTO)/ZnO compact layer/Sb_2S_3 NR grown on ZnO NF/P3HT/MoO_x/Ag was prepared, a highest PCE of 0.662% was attained. The rectification ratio and photocurrent generation efficiency of the comb-shaped Sb_2S_3 nanorod arrays were improved as compared with the heterojunction of randomly stacked Sb_2S_3 nanorods. Smaller series resistance (R_s) of 8.13 Ω cm^{-2} and an ideality factor (n) of 2.84 with the comb-shaped Sb_2S_3 nanorod arrays than those of the randomly stacked ones of R_s = 15.01 Ω cm^{-2} and n = 3.83 also indicated superior charge extraction property and suppressed recombination of the comb-shaped Sb_2S_3 nanorod arrays at the interface.

In conclusion, this thesis verifies the superiority of carrier transport along the $(Sb_4S_6)_n$ nanoribbons in [001] direction. A facile wet method was firstly introduced in this work that can be widely used to grow highly [001] oriented Sb_2S_3 or Sb_2Se_3 nanorods on preferred substrate. In this wet method, the amount of PVP is crucial to control the geometric shape of fabricated nanorods, and thus control the optical and electrical properties of the nanorod arrays. This work also provides a new perspective for the combination of Sb_2S_3 and Sb_2Se_3 after verified the crystal structure similarity between them. The optimization of Sb_2S_3 nanorod arrays based solar cells and Sb_2S_3 nanorod arrays/Sb_2Se_3 nanorod arrays based solar cells were also discussed. Also, the possibility of making hierarchical composite nanostructured Sb_2S_3 material was discovered by introducing a comb-shaped Sb_2S_3 nanorod arrays growing on ZnO nanofibers.

References

1. Versavel, M. Y., Haber, J. A., Structural and optical properties of amorphous and crystalline antimony sulfide thin-films, *Thin Solid Films*, **2007**, 515, 7171-7176.
2. Kondrotas, R., Chen, C., Tang, C., Sb_2S_3 solar cells, *Joule*, **2018**, 2, 857–878.
3. Zakaznova-Herzog,V. P., Harmer, S. L., Nesbitt, H. W., High resolution XPS study of the large-band-gap semiconductor stibnite (Sb_2S_3): Structural contributions and surface reconstruction, *Surface Science*, **2006**, 600(2), 348-356.
4. Zhou, Y., Leng, M. Y., Xia, Z.,. Solution-Processed Antimony Selenide eterojunction Solar Cells, *Advanced Energy Materials*, **2014**, 4(8), 1301846.
5. Savadogo, O., Mandal, K. C., Low Cost Schottky Barrier Solar Cells Fabricated on CdSe and Sb2S3 Films Chemically Deposited with Silicotungstic Acid. *Journal of the Electrochemical Society*, **1994**, 141(10), 2871-2877.
6. Savadogo, O., Mandal, K. C., Low-cost technique for preparing n-Sb_2S_3/p-Si hetero-junction solar cells, *Applied Physics Letters*, **1993**, 63(2), 228-230.

7. Abd-El-Rahman, K. F., Darwish, A. A., Fabrication and electrical characterization of p-Sb_2S_3/n-Si heterojunctions for solar cells application, *Current Applied Physics*, **2011**, 11(6), 1265-1268.
8. Escorcia-García, J., Becerra, D., Nair, M. T. S., Heterojunction CdS/Sb_2S_3 Solar Cells Using Antimony Sulfide Thin Films Prepared by Thermal Evaporation, *Thin Solid Films*, **2014**, 569, 28-34.
9. Lei, H., Yang, G., Guo, Y., Efficient planar Sb_2S_3 solar cells using a low-temperature solution-processed tin oxide electron conductor, *Physical Chemistry Chemical Physics*, **2016**, 18(24), 16436-16443.
10. Kim, D. H., Lee, S. J., Park, M. S., Highly Reproducible Planar Sb_2S_3-sensitized Solar Cells Based On Atomic Layer Deposition. *Nanoscale*, **2014**, 6(23), 14549-14554.
11. Zimmermann, E., Pfadler, T., Kalb, J., Toward High-Efficiency Solution-Processed Planar Heterojunction Sb_2S_3 Solar Cells, *Advanced Science*, **2015**, 2(5), 150059.
12. You, M. S., Lim, C. S., Kwon, D. H., Oxide-free Sb_2S_3 sensitized solar cells fabricated by spin and heat-treatment of Sb(III)(thioacetamide)$_2$Cl$_3$, *Organic Electronics*, **2015**, 21, 155-159.
13. Kamruzzaman, M., Chaoping, L., Yishu, F., Atmospheric annealing effect on TiO_2/Sb_2S_3/P3HT heterojunction hybrid solar cell performance, *RSC Advances*, **2016**, 6(101), 99282-99290.
14. Ma, X., Zhong, J., Li, M., Hybrid solar cells using solution-processed TiO_2/Sb_2S_3 bilayer as electron transport layer, *Solar Energy*, **2016**, 133, 103-110.
15. Chen, X., Li, Z., Zhu, H., CdS/Sb_2S_3 heterojunction thin film solar cells with a thermally evaporated absorber, *Journal of Materials Chemistry C*, **2017**, 5(36), 9421-9428.
16. Lan, C., Liang, G., Lan, H., Microstructural and optical properties of Sb_2S_3 film thermally evaporated from antimony pentasulfide and efficient planar solar cells. *physica status solidi-Rapid Research Letters*, **2018**, 12(6), 1800025.
17. Li, S., Zhang, Y., Tang, R., Aqueous-Solution-Based Approach Towards Carbon Free Sb_2S_3 Films for High Efficiency Solar Cells, *ChemSusChem*, **2018**, 11(18), 3208-3214.
18. Zhang, Y., Li, S. A., Tang, R., Phosphotungstic Acid Regulated Chemical Bath Deposition of Sb2S3 for High-Efficiency Planar Heterojunction Solar Cell, *Energy Technology*, **2018**, 6(11), 2126-2131.
19. Jin, X., Yuan, Y., Jiang, C., Solution processed NiOx hole-transporting material for all-inorganic planar heterojunction Sb_2S_3 solar cells, *Solar Energy Materials and Solar Cells*, **2018**, 185, 542-548.
20. Zhang, L., Jiang, C., Wu, C., V_2O_5 as Hole Transporting Material for Efficient All Inorganic Sb_2S_3 Solar Cells. *ACS Applied Materials & Interfaces*, **2018**, 10(32), 27098-27105.
21. Jiang, C., Tang, R., Wang, X., Alkali Metals Doping for High-Performance Planar Heterojunction Sb_2S_3 Solar Cells, *Solar RRL*, **2019**, 3(1), 1800272.

22. Yin, Y., Wu, C., Tang, R., Composition engineering of Sb_2S_3 film enabling high performance solar cells, *Science Bulletin*, **2018**, 64(2), 136-141.
23. Tang, R., Wang, X., Jiang, C., Vacuum assisted solution processing for highly efficient Sb_2S_3 solar cells, *Journal of Materials Chemistry A*, **2018**, 6(34), 16322-16327.
24. Liu, R., Shen, Z., Wan, Z., Nanoarray heterojunction and its efficient solar cells without negative impact of photogenerated electric field, *Communications Physics*, **2021**, 4(1), 1-12.