Elemental Doping—An Effective Method to Improve Semiconductor Thin-film Solar Cells Efficiency

Mingyan Ma^{1,*}, Guodong Xu²

¹Department of Maritime and Transportation, Ningbo University, Ningbo, 315832, China ²College of Materials Science and Engineering, Anhui University of Science and Technology, Huainan, 232001, China *Corresponding author: 18645143107@139.com

Keywords: Semiconductor Thin-film Solar Cell, Elemental Doping, Band Gap Width

Abstract: Nowadays, energy constraints and environmental problems are becoming increasingly serious. Semiconductor thin-film solar cells are widely used due to their green, simple operation and easy maintenance and so on. Elemental doping can enhance the semiconductor conductivity, raise the selectivity and activity of catalysts, and improve the microstructure of materials. It is widely regarded as an important way to increase the efficiency of solar cells. In this paper, the effect of elemental doping on the performance of perovskite solar cells, organic thin film and inorganic thin film solar cells is studied. Elemental doping can improve the electrical and photovoltaic performance of the cell. The carrier migration rate is improved after doping, thereby increasing the carrier lifetime. In addition, the morphology is improved by reducing surface defects. Compaction is improved due to increased grain size and reduced porosity. Most importantly, this method can improve energy utilization and promote the development of renewable energy sources.

1. Introduction

Nowadays, fossil fuels have limited energy storage and release large amounts of pollutant gases when burned, causing harm to the environment. Therefore, new types of clean and non-polluting batteries have emerged. Solar cells are widely used because of the advantages of no noise, no pollution and easy-to-use[1].

The principle of solar cells is mainly based on the photoelectric effect. Specifically, the semiconductor in a solar cell absorbs light energy and then excites free electrons and free holes. They generate a difference in electric potential and finally an electric current. Traditional solar cells can be divided into perovskite solar cells, silicon-based solar cells, and so on. Lower efficiency is their main drawback. Conventional solar cells normally have a conversion efficiency of between 10 and 20 percent. This means that only a small portion of the solar energy is converted into usable electricity. Therefore, it is particularly important to modify these conventional solar cells to improve their performance [2].

Elemental doping is a method of altering the properties of a material by doping certain elements into the material. It can change the microstructure of the material and improve its properties, thereby increasing the efficiency of utilization[3]. In a microscopic sense, elemental doping can change the

semiconductor band gap width, reduce the inverse defects of solar cells, and improve its microstructural performance. Besides, it can promote grain growth, improve the grain size, and reduce the thickness of the fine-grain layer. Meanwhile, it increases the carrier mobility rate, and improves the device performance. In the macro sense, high-performance materials with high strength, high hardness and corrosion resistance can be prepared by elemental doping. In addition, the optical and electrical properties of the doped material can be improved. Therefore, elemental doping is a promising method of material modification with a wide range of applications[4].

This paper investigates the effect of various elemental doping on the efficiency of semiconductor thin film solar cells. It is found that doping significantly increases the device voltage, current density and conversion efficiency. Alkaline element doping can change parameters such as electron and hole mobility, energy level structure, and band gap width in the material. This method can increase the battery short-circuit current and open-circuit voltage, and then improve the photoelectric conversion efficiency and stability of the battery. Ion doping can improve the transport properties of carriers and charge lifetime of the material, and improve the electrical properties of the material and increase its efficiency. In semiconductor thin-film solar cells, elemental doping can improve photovoltaic conversion efficiency and reliability, and has important application significance[5].

2. Elemental doping of several solar cells

2.1 Perovskite solar cells

The function of elemental doping for perovskite solar cells is mainly to boost the properties and their stability. The electrical configuration and the optical characteristics of the perovskite material can be changed by doping with metal elements. This can improve the conversion effectiveness, stability and lifetime of perovskite solar cells.

Ayyakannu Sundaram Ganeshraja et al. doped multielement reddish rutile titanium dioxide nanocrystalline electronic transmission layer into perovskite solar cell. The photovoltaic performance was improved after doping. In addition, as shown in Fig. 1(a), the efficiency of the PSC reaches 10.4% with 0.01% doping of AgCl@Sn-TiO₂. Compared with the PSC with undoped TiO₂ (10.0%) ETL (Fig. 1(b)), the device has higher stability over 650 hours[6]. Yurong Jiang et al. tuned the polarization of the hole transmission layer by adding metal-like MoO_x to PEDOT: PSS. Subsequently, the effects of interfacial poling on the photovoltaic properties in hybrid PSC devices was investigated. Trace amounts of MoO_x resulted in significantly enhancing of the electric conduction in PEDOT: PSS HTL. It also promotes hole extractions, transmissions and collecting from perovskite active layer to the ITO anode. And it leads to enhance the interfacially attracted polarisation between PEDOT: PSS HTL and the perovskite anode. The short-circuit current density (JSC) increases from 17.75 mA/cm² to 19.64 mA/cm². The open-circuit voltage (VOC) increases from 0.96 V to 1.01 V. The FF improves from 0.65 to 0.76 as shown in Fig. 1(c), and the PCE enhances significantly by 15.01%[7]. Zonglong Song et al. doped various lanthanide ions into perovskite films to greatly improve the performance of PSC. The particle dimension of perovskite films increased and crystallinity increased with the Ln³⁺ doped, resulting in a remarkable improvement in the effectiveness and stability of the polystyrene composites. The Ce³⁺ doped PSCs have the best performance as shown in Fig. 1(d). Correspondingly, its champion power conversion efficiency (PCE) increased up to 21.67% from 18.50% [8].

Metal element doping improves the conductivity and photovoltaic performance in solar cells. In addition, they have their own unique characteristics. For example, Mo doping induces an interfacial polarized electric field. This promotes charge separation as well as complexation between shielding traps and free charges. Sn doping enhances the visible photocatalytic activity of titanium dioxide. AgCl-loaded and Sn-doped units are responsible for plasma and photoinduced electron capture.



Figure 1: Performance tests of fuel cells. (a) Photovoltaic efficiency of the perovskite solar cell; (b) Stability spectrum of the undoped TiO₂ and AST-0.01 photoelectrodes; (c) Fill factor of the perovskite solar cell; (d) Forward and reverse J-V curves of PSCs

2.2 Organic thin film solar cells

Elemental doping can improve the light absorption property in organic thin film solar cells, increase the carrier injection and transport capacity, reduce energy loss, and inhibit charge recombination, thereby increasing the efficiency of organic solar cells.

Danqin Li et al. doped n-type DMBI-BDZC into a binary heterojunction (BHJ) photoactive layer consisting of a polymer donor, PM6, and a non-fullerene acceptor, Y6, in an organic solar cell (OSC). DMBI-BDZC has electrodoped the Y6 constituent of BHJ mixture, and this doping procedure remarkably enhanced and balanced the mobility of charge carriers. It improved exciton dissociation and increased carriers lifetime. It also inhibited charge recombination by reducing the energy loss in the heterojunction. Champion OSC devices with PCE up to 18.33% and FF up to 80.20% were finally achieved as shown in Fig. 2(a). The device has excellent stability [9]. Zinc oxide thin films treated by sol-gel method were used as electron buffer layer (EBL) for inverted organic solar cells by Muhammad Zafar et al. Thiophene was chosen as a sulphur dopant for doping in the films. The PCE of the organic solar cell was observed to be 4.16% when the ZnO film thickness was 25 nm and the sulfur doping rate was 4 at%. As shown in Fig. 2(d), the PCE was improved by 10% in comparison with the referenced device. In addition, the PCE of the 4 at% sulfur doped ZnO EBL device remains at 74% of the original value for 264 h, as in Fig. 2(b). This shows that it is more stable than the referenced ZnO device[10]. Xin Song et al. modified the optoelectronic and morphological characteristics of zinc oxide layers by zirconium (Zr) doping. Zirconium doping not only increased the transmittance, but also optimised the surface morphology. This improved the charge extraction performance and reduced the possibility of charge trapping-assisted compounding. The maximum power conversion efficiency (PCE) of the PM6: Y6: PC71BM solar cell device was as high as 17.2% using ZnO: Zr as the ETL inverted device structure. This improvement is 9.55% Compared with the device with undoped ZnO ETL, as shown in Fig. 2(c)[11].

Therefore, both electrical doping and metal element doping can increase the carrier mobility and enhance its electron transport properties. They also extend the carrier lifetime by reducing energy loss. Finally, the photocatalytic activity is enhanced by elemental doping. The surface morphology also becomes more uniform. Elemental doping can effectively change the optical and electronic properties of chromated solar cells.



Figure 2: Performance tests of fuel cells. (a) PM6:Y6 based binary OSCs of reported previously and this work; (b) Power-conversion efficiency of IOSCs with ZnO and S-ZnO; (c) The box plots for PCEs; (d) $(\alpha hv)^2$ vs photon energy for ZnO and S-ZnO films

2.3 Inorganic thin film solar cells

Elemental doping can change the band gap width of inorganic thin film solar cells. It increases the photogenerated carrier transport efficiency and distance. Improvement of the surface structure and strength of the material to increase the stability of the device and the service life. Ultimately, the effectiveness of the solar cells is improved.

Junye Tong et al. used a dual-ion doping strategy to improve the surface microstructure and device performance of solar cells. The particle dimension increased significantly after doping, the thickness of the fine grain layer was reduced, and the performance was improved. Moreover, the PCE of CZTSSe solar cells when doped with single ions of Li⁺, Ag⁺ and Cd²⁺ were 7.60%, 7.99% and 7.11%, respectively, compared with the conventional method (6.18%). The PCE increased to 8.87% when doped with Li⁺&Ag⁺ ions and 8.39% when doped with Li⁺&Cd²⁺[12]. Lixin Zhang et al. obtained highly efficient devices by doping Li in air into CZTSSe films. The crystal quality was improved

after doping, and a full and dense absorption layer crystal was achieved. In addition, as shown in Fig. 3(a), the attenuation time for the doped samples increased from the original 2.23 ns to 3.63 ns, resulting in a significant improvement in the carrier lifetime of CZTSSe. Li-doped CZTSSe thin-film solar cells ultimately achieved a high-efficiency of 9.84% [13]. Tianyue Wang et al. synthesised CZTSSSe thin films on soda lime glass substrates by replacing tin atoms in the crystals with antimony doping, followed by sol-gel and two-step annealing techniques. A moderate doping of antimony can promote the particle growth and prepare dense films with larger particle dimensions and smaller holes. Replacing tin sites with antimony reduces the generation of harmful defects associated with tin.As shown in Fig. 3(b), the open-circuit voltage (VOC) of the CZTSSSe (Sb=0.10) device is improved with 29 mV over the original device. The power conversion efficiency (PCE) is increased up to 6.82% from 5.06% [14].

Sb doping results in increased carrier mobility and improved electrical properties. At the same time, the surface morphology is enhanced. Li doping improves the crystal quality. Carrier lifetime is significantly increased. The surface morphology is less porous and denser. Li⁺&Ag⁺ and Li⁺&Cd²⁺ bi-ionic doping can passivate defects and regulate the band gap, as well as promote crystal growth.



Figure 3: Performance tests of CZTSSSe. (a) Time resolved photoluminescence decay curves for Li-doped and undoped CZTSSe films; (b) J-V curves of the CZTSSSe

3. Conclusions

In summary, this paper explores the effects of doping on solar cell performance. Results show element doping can effectively enhance and balance the charge carrier mobility of organic thin-film solar cells, improve the exciton dissociation, and extend carrier lifetime. Element doping can improve the conductivity and photovoltaic properties of perovskite solar cells, and then reduce energy loss and inhibits charge complexation. Elemental doping can also significantly improve the electrical properties and crystal quality of inorganic thin film solar cells. Most importantly, this method brings more possibilities for semiconductor thin-film solar cell development.

References

[1] Wang J, Liu L, Zhao M, et al. Graphdiyne oxide modified nano CuO as inorganic hole transport layer for efficient and stable organic solar cells[J].2D Materials, 2021, 8(4):044015 (8pp).DOI:10.1088/2053-1583/ac2a92.

[2] Zainun A R, Mamat M H, Noor U M, et al. Characterization of Copper (I) Iodide (CuI) Thin Film using TMED for Dye-Sensitized Solar Cells[J]. Advanced Materials Research, 2013, 667:447-451. DOI:10.4028/www. Scientific .net/AMR.667.447.

[3] Xiao Z, Yuan Y, Wang Q, et al. Thin-film semiconductor perspective of organometal trihalide perovskite materials for high-efficiency solar cells[J]. Materials Science and Engineering: R: Reports, 2016.DOI:10.1016/j.mser.2015.12.002.
[4] Nakano K, Usui T, Takayashiki Y, et al. PB58 Evaluation of Carrier Collection Efficiency of Organic Thin-film Solar

Cells with a Calamitic Liquid Crystal[J].Proceedings of Japanese Liquid Crystal Society Annual meeting, 2013:_PB58-1 - PB58-2.DOI:10.11538/ekitou.2013.0 PB58.

[5] Xue C R, Sun X Y. High Efficiency Thin Film Silicon Solar Cells[J]. Advanced Materials Research, 2013, 750-752:970-973. DOI: 10.4028/www.scientific.net/AMR.750-752.970.

[6] Kalytchuk S, Gupta S, Zhovtiuk O, et al.Semiconductor Nanocrystals as Luminescent Down-Shifting Layers To Enhance the Efficiency of Thin-Film CdTe/CdS and Crystalline Si Solar Cells[J].Journal of Applied Physics, 2014, 118(30):16393–16400.DOI:10.1021/jp410279z.

[7] Ausserlechner S J, Gruber M, Hetzel R, et al. Mechanism of surface proton transfer doping in pentacene based organic thin-film transistors[J]. Physica Status Solidi, 2011, 209(1):181-192. DOI:10.1002/pssa.201127595.

[8] Liu X, Zi W, Liu S.p-Layer bandgap engineering for high efficiency thin film silicon solar cells[J]. Materials Science in Semiconductor Processing, 2015, 39:192-199. DOI: 10.1016/j.mssp.2015.04.011.

[9] Schulze T F, Korte L, Conrad E, et al. High-forward-bias transport mechanism in a-Si: H/c-Si heterojunction solar cells[J]. Physica Status Solidi, 2010, 207(3):657-660. DOI: 10.1002/pssa. 200982747.

[10] Zhang J, Jia M, Sales M G, et al.Impact of ZrO2 Dielectrics Thickness on Electrical Performance of TiO2 Thin Film Transistors with Sub-2 V Operation[J].ACS Applied Electronic Materials, 2021.DOI:10.1021/acsaelm.1c00909.

[11] Chen Y H, Liu Y T, Huang C F, et al. Improved photovoltaic properties of amorphous silicon thin-film solar cells with an un-doped silicon oxide layer [J]. Materials Science in Semiconductor Processing, 2015, 31:184-188. DOI: 10.1016/j. mssp.2014.11.042.

[12] Park S, Yong Ji H, Jun Kim M, et al. Enhanced quantum efficiency of amorphous silicon thin film solar cells with the inclusion of a rear-reflector thin film[J]. Applied Physics Letters, 2014, 104(7):073902-073902-5. DOI: 10. 1063/1. 4865927.

[13] Zeng K, Xue D J, Tang J.Antimony selenide thin-film solar cells[J].Semiconductor Science & Technology, 2016, 31(6):063001.DOI:10.1088/0268-1242/31/6/063001.

[14] A P L, B S E Y, A Y M, et al. Design of Ag nanograting for broadband absorption enhancement in amorphous silicon thin film solar cells[J]. Materials Science in Semiconductor Processing, 2015, 39:760-763. DOI:10.1016/j. mssp. 2015. 06.047.