ISSN 2959-6157

Modification of New Semiconductor Materials by Doping

Yixiang Huang[1, *]

[1]College of Material Science and Engineering, Nanjing Forestry University, Nanjing, China
*Corresponding author: spacex@njfu.edu.cn

Abstract:

In the era of information, people's lives are inseparable from electronic equipments. Semiconductors are key materials for manufacturing electronic equipment, which can be applied in multiple fields such as integrated circuits, solar cells, and so on. However, pure semiconductors have a single property, which are difficult to meet the design and usage requirements of different electronic devices. To solve the problem, introducing heteroatoms for modification to make them have more suitable performance will be a good way. Good semiconductor performance generally relies on precise control of the doping process. Different types of semiconductor materials typically require specific doping techniques to improve its performance. Adding small amounts of heteroatoms to pure semiconductors can significantly improve their conductivity by forming p/n junctions or achieving specific functions. Doping technology has been widely used in the semiconductor manufacturing industry. It is of great significance for the manufacturing of chips, photovoltaics and other devices. At present, there are still many shortcomings in doping technology. It may come across the semiconductor structure failure caused by doping, or difficulty in meeting performance requirements for use. Thereofore, continuous research and improvement are still needed. This paper reviewed the applications and the doping techniques of various semiconductor materials including two-dimensional semiconductors and organic semiconductors. In addition, it also provides prospects for their related applications and development.

Keywords: New semiconductor; doping; p-n junction; bandgap; solar cell.

1. Introduction

Semiconductors, a material whose conductivity is between conductors and insulators, play a significant role in the application of photoelectricity, communication, healthcare, and other fields. Since its appearance, semiconductor materials have undergone generation after generation of improvements. In the 1950s, silicon and germanium developed into the first generation of semiconductor materials. However, the narrow bandgap, low electron mobility, and breakdown electric field of silicon materials limited their applications. Later, the second generation of semiconductors, mainly compound semiconductors, was born, which had better performance than the first generation. After entering the 21st century, wide bandgap semiconductors have become the third generation of semiconductors and have been widely used. At present, semiconductor is still a research hotspot. The two-dimensional semiconductor materials, organic semiconductor materials, and semiconductor nanocomposites, which will be discussed in this paper, are all new semiconductor materials under study. New semiconductor materials exhibit more outstanding performance in conductivity and stability. However, pure semiconductors are difficult to show performance that meets usage requirements. Therefore, doping techniques are needed for modification.

In order to enhance the conductivity of semiconductors and improve efficiency, dopants are usually added to semiconductors. Doping is a method of introducing a small amount of heteroatoms into the semiconductor to alter its electrical properties. These heteroatoms replace or occupy the positions of some atoms in the semiconductor lattice, thereby changing its performance. Introducing dopants can activate neighbour electrons and holes, thereby forming p-type or n-type semiconductors. Adding P, As with 5 valence electrons to Si semiconductor can produce n-type semiconductor, while adding B, Ga with 3 valence electrons can produce p-type semiconductor. Those doped semiconductors can generate different properties and junctions, which can be applied in various electronic devices such as diodes, transistors, solar cells, and so on. For example, p-type semiconductor doping can increase the energy transfer efficiency of perovskite solar cells by 30% [1]. Different types of semiconductors may fit different doping processes, and many semiconductor materials, especially two-dimensional materials, still lack efficient doping methods. This is largely due to the damage caused by doping processes to the materials and structural distortion [2]. The doping methods widely used in the silicon industry, ion implantation and thermal diffusion, generally have problems. For example, some doping methods have limited applicability in some systems [3]. Therefore, exploring how to achieve doping in new semiconductor materials which include two-dimensional semiconductor materials, organic semiconductor materials, and semiconductor nanocomposites materials, has important research value. In this paper, the doping techniques, research status, and mechanisms of new semiconductors will be reviewed. Afterwards, the advantages and disadvantages of different doping techniques will be compared. Moreover, the future development directions of this area will also be discussed.

2. Doping of Two-dimensional Semiconductor Materials

Two-dimensional material means layered materials with the thickness as small as the nanometer scale in one direction They can also stand for planar materials where electrons can only move in two directions. A typical two-dimensional material is graphene, which can be used in batteries and catalysis. In 2004, the scientific research team of Manchester University used tape to mechanically separate graphene monomer. From then on, two-dimensional materials represented by graphene have developed rapidly. Many two-dimensional materials have electronic transfer properties and can be used to make semiconductor materials. After doping, they will form p/n type semiconductors, which are widely used in many fields such as communication, chips, and optoelectronic devices [4]. However, doping may also damage the crystal structure of semiconductors and cause material failure. It is crucial to seek suitable doping methods in two-dimensional semiconductors. Understanding the doping mechanism of two-dimensional semiconductors can help improve their performance. Bandgap control and self doped p-n junction are effective means of doping in two-dimensional semiconductors.

2.1 Bandgap Control in Two-dimensional Semiconductors

According to band theory, there is a bandgap between the valence and conduction bands of a semiconductor. The size of the bandgap determines the level of the conductivity of semiconductor. In the application of semiconductor materials, it is often necessary to control the size of the bandgap to adapt to different usage requirements. Introducing doped atoms is an effective method to control the bandgap size. For example, a monolayer of tungsten disulfide is integrated into a self-assembled plasmonic crystal by coherent doping of plasma hot electrons. Coherent coupling is established between semiconductor excitons and plasmon resonances, which can control the bandgap of two-dimensional semiconductor materials [5].

2.2 Self Doped p-n Junction of Two-dimensional Materials

According to the different carriers, semiconductors are divided into p-type semiconductors and n-type semiconductors. Most carriers in p-type semiconductors are holes, while most carriers in n-type semiconductors are electrons. Generally, intrinsic semiconductors can only form p/n-type semiconductors by introducing heteroatoms. However, in 2020, the team led by Dai Ying from Shandong University discovered the phenomenon of self doped p-n junctions in 2D materials. Under the built-in electric field of layered In_2X_3, a three-layer In_2X_3 can form a self doped p-n junction without external regulation [6]. Self doped p-n junction is a kind of p-n junction that can be formed without introducing heteroatoms. Van der Waals materials formed by stacking two-dimensional layered atoms can form self doped p-n junctions by increasing or decreasing the number of layers. This new technology can solve the problem of low efficiency in traditional doping techniques. Traditional doping techniques generally introduce heteroatoms into semiconductors, but introducing heteroatoms may damage the original semiconductor structure. Heteroatoms need to be localized to specific areas to achieve the desired effect. Therefore, traditional doping often faces the risks of instability and low efficiency. The p-n junction formed by self doping avoids the introduction of heteroatoms. Therefore, this layer p-n junction can be used to reduce the functional failure of semiconductor materials caused by doping atoms not being localized in designated areas [2]. The discovery of self doping phenomenon in two-dimensional semiconductors may redefine semiconductor structures, enabling the next generation of semiconductor materials to be made smaller, more efficient, and more stable. However, two-dimensional semiconductor materials still face problems such as easy to oxidize and difficult production processes, which still need further investigations.

3. Doping of Organic Semiconductor Material

Organic semiconductor materials are organic materials with semiconductor properties, which are widely used in industry due to their low cost and stretchability. Organic semiconductors can be divided into three categories including polymers, organic compounds, and donor acceptor complexes. It can also be classified into small molecule organic semiconductor materials and polymer organic semiconductor materials based on their molecular weight. To a certain extent, organic semiconductors have developed based on inorganic semiconductors, so the classification mechanism is similar. Doping heteroatoms into the materials is an effective method to improve the carrier concentration in organic semiconductors. However, the charge transfer ability of organic semiconductors is still relatively low when compared to inorganic semiconductors. Therefore, efficient doping techniques need to be developed to change conductivity. Organic semiconductors participate in the entire process of charge activity in the application of optoelectronic devices. In many recent studies, new doping techniques are being sought. For example, it's reported that molecular doping has the potential to act as an enabler due to various synergistic effects, which can further improve the related technologies of organic semiconductor doping. Besides, Lewis acid doping technology can also affect the electronic transport of organic semiconductors through different pathways [7]. At present, further research is needed on the physical properties such as Fermi level and crystal structure of doped organic semiconductors.

3.1 Doping Technology of Organic Semiconductors

Organic semiconductor doping is an important step in achieving good performance, and the following two doping methods will be introduced.

The main carrier of n-type semiconductors is electrons which are provided by heteroatoms, while holes are minority carriers formed by thermal excitation. Due to the influence of doping efficiency, n-type organic semiconductors often have lower conductivity compared to p-type semiconductors. Therefore, further research is needed on doping n-type organic semiconductors. DMBI-H derivatives are the most widely used n-type dopants. The transfer of hydrides to organic semiconductors is considered to be the most likely determining step of reaction rate during n-doping process. The specific thermodynamic and kinetic data of doping can be calculated through density functional theory. Through this way, the most suitable dopant and doping method can be selected [8]. In addition, Lewis base anions are also effective dopants. In this case, the interaction between the electron donating ability of base anions and the electron affinity of π-acceptors, contribute to complete electron transfer [9]. This is a relatively moderate doping process that can be applied in various fields such as field-effect transistors and solar cells.

Traditional doping processes are mostly chemical doping, relying on the activity of dopants. During the doping process, dopants are constantly consumed, resulting in lower doping efficiency for weakly active dopants. In recent research on organic semiconductor catalytic doping, a research team has discovered a photocatalytic doping method that uses organic photocatalysts as carriers and air as weak oxidants to achieve p-type doping. This method can solve the problems of poor stability and low efficiency of dopants [10]. Photocatalytic doping can also be coupled with p-type/n-type semiconductor doping to enable complementary doping of p-type/n-type organic semiconductors without consuming any oxidants or reducing agents. This technology is expected to show significant application value in the semiconductor and electronics industries.

3.2 Application of Organic Semiconductor Doping in Solar Cells

Organic semiconductors are widely used in the production of solar cells, which generally have a multi-layer structure including conductive substrate, photovoltaic active layer, electron transport layer, and the vacuum deposited layer. The current transport layer of organic solar panels is generally organic semiconductor material, and the doped transparent transport layer can sandwich the photovoltaic active layer in the middle to approach the ideal solar cell structure proposed by Wurfel [11]. The position of the Fermi level can be controlled by the doping of the transport layer, thus providing more freedom in the selection of electrode materials, sequences, and optical optimization [12]. In short, organic semiconductor doping will provide new directions for the development of future solar cells.

4. Doping of Semiconductor Nanocomposites

Nanocomposite materials refer to composite materials formed by dispersing nanoscale modifiers into a continuous matrix through specific methods. Semiconductor nanocomposites are nanocomposites with semiconductor properties. It is a multiphase solid material that produces comprehensive properties through the synergistic effects between components. Semiconductor nanocomposites possess many special properties and functions that conventional materials do not have. Similar to other semiconductors, semiconductor nanocomposites require the introduction of dopants for stabilization. There are currently many doping techniques under study. Among them, utilizing the instability doping of metal halide perovskites is an important research direction. At 450°C, $CsPbBr_3$ perovskite is converted to Cs_4PbBr_6 in the presence of PbS to produce nanocrystalline composites doped with Cs_4PbBr_6 nanoprecipitates. This new doping strategy can adjust the carrier density within a certain range [13]. It is generally applicable to other semiconductors based on nanocrystals. In addition, Co doped ZnO semiconductor nanocomposites with Au nanoparticles are beneficial for improving the separation efficiency between electrons and holes in semiconductors under the condition of visible light excitation.

This doping is expected to achieve quantum effects to promote the development of surface enhancement Raman scattering (SERS) substrates in the future [14]. Semiconductor nanocomposites have broad application prospects in fields such as optoelectronic devices and photocatalytic hydrogen production. However, in practical applications, it is necessary to select suitable materials and dopants according to specific needs.

5. Conclusion

The performance of semiconductor materials depends on semiconductor doping technology. Efficient doping technology can promote the development of semiconductor materials and simplify semiconductor manufacturing processes. It can also provide new ideas for the manufacturing of next-generation integrated circuits. Specific semiconductors often require specific doping processes. In this paper, the relevant doping processes and mechanisms are summarized. Doping techniques in two-dimensional semiconductor materials, organic semiconductor materials, and semiconductor nanocomposites materials are discussed in detail. Further improvements are still needed in reducing manufacturing costs, improving stability and efficiency in the future.

References

[1] Zhou Zhongmin, Qiang Ziyue, Takumi Sakamaki, et al. Organic/Inorganic hybrid p-Type semiconductor doping affords hole transporting layer free thin-film perovskite solar cells with high stability. ACS Applied Materials&Interfaces, 2019, 11(25): 22603-22611.

[2] Xia Hui, Luo Man, Wang Wenjing, et al. Pristine PN junction toward atomic layer devices. Light: Science & Applications, 2022, 11(7): 1515-1522.

[3] Wang Yanan, Zheng Yue, Han Cheng, et al. Surface charge transfer doping for two-dimensional semiconductor-based electronic and optoelectronic devices. Nano Research, 2021,14: 1682-1697.

[4] Li Songyu, Liu Famin, Ma Yang, et al. p-/n-Type modulation of 2D transition metal dichalcogenides for electronic and optoelectronic devices. Nano Research, 2022,15(1): 123-144.

[5] Chen Yuhui, Tamming R R, Chen K, et al. Bandgap control in two-dimensional semiconductors via coherent doping of plasmonic hot electrons. Nature Communications, 2021, 12(1):4332.

[6] Peng Rui, Ma Yandong, Zhang Shuai, et al. Self-doped p-n junctions in two-dimensional In_2X_3 van der Waals materials. Materials Horizons, 2020, 2: 504-510.

[7] Alberto D Scaccabarozzi, Aniruddha Basu, Filip Aniés, et al. Doping approaches for organic semiconductors. Chemical Reviews, 2021, 122(4): 4420-4492.

[8] Xu Chunlin, Wang Dong. Electron transfer driving force as the criterion for efficient n-doping of organic semiconductors with DMBI-H derivatives. Journal of Materials Chemistry A, 2023, 11, 15416-15425.

[9] Jiang Danni, Yan Kangrong, Li Changzhi. Doping of organic semiconductors with Lewis base anions: Mechanism, Applications and Perspectives. Acta Chimica Sinica, 2020, 12: 1287-1296.

[10] Jin Wenlong, Yang Chiyuan, Riccardo Pau, et al. Photocatalytic doping of organic semiconductors. Nature, 2024, 630: 96-101.

[11] Peter Würfel. Photovoltaic Principles and Organic Solar Cells. Chimia, 2007, 61(12): 770-774 .

[12] B. Lu ssem, M Riede, K Leo. Doping of organic semiconductors. Physica Status Solidi (A), 2013, 210: 19-43.

[13] Mariano Calcabrini, Aziz Gençet, Liu Yu, et al. Exploiting the lability of metal halide perovskites for doping semiconductor nanocomposites. ACS Energy Letters, 2021, 6(2): 581-587.

[14] Zhai Yan, Zhao Xiaoyu, Ma Zhiyuan, et al. Au nanoparticles (NPs) decorated Co doped ZnO semiconductor (Co400-ZnO/Au) nanocomposites for novel SERS substrates. Biosensors, 2022, 12(12): 1148.