Preparation of Selenide Semiconductor Materials and Photoelectric Detection in Thin Film Solar Cells

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Abstract. For nearly half a century, semiconductor technology has achieved rapid development as the core of modern high technology. New materials and various functional devices based on semiconductor technology affect all aspects of national production and life. The development and application of semiconductor materials is the basis for the development of semiconductor technology, which is also an important source of motivation and confidence for countless researchers. In this paper, two kinds of selenide semiconductors with excellent material properties are selected for key research, including the controllable preparation of materials and the exploration of high-performance optoelectronic functional devices. Firstly, Sb2Se3 nanorods were prepared by thermal injection method, and the key defects of low conductivity of Sb2Se3 nanorods were successfully solved by forming semiconductor heterojunction and semiconductor doping. Based on this, a Sb2Se3 nanorod-based photovoltaic with excellent performance was constructed. Prototype device. Subsequently, the conductivity and photoconductivity of Sn-doped Sb2Se3 polycrystalline semiconductor were controlled by high-temperature melting method. Based on the preparation of Sb2Se3-based target, Sb2Se3-based thin film was prepared by RF magnetron sputtering. Quasi-homojunction Sb2Se3 thin film solar cell with important development potential. In addition, the thermal injection method is used to realize the controllable preparation of pure phase nanoflowers, and combined with mature Si-based semiconductor technology, the high-performance y-Iri2Se3/Si heterojunction photodiode is constructed for the first time.

1. Introduction

First, we need to understand some basic knowledge of semiconductor materials. A semiconductor is a kind of functional material with a conductivity between the conductor and the insulator. It mainly conducts electricity by electrons in the conduction band or holes in the valence band. When exposed to external light, heat or doping into trace impurities, The conductivity is usually changed significantly. There are many types of semiconductor materials, which are generally classified into three categories: elemental semiconductors, inorganic compound semiconductors, and organic compound semiconductors depending on the chemical composition of the materials. Among them, elemental semiconductors include 11 kinds of elements with semiconductor characteristics. Due to the stability of the elements themselves and the limitations of the preparation process, only Ge, Si, and Se are currently available. The inorganic compound semiconductor can be further classified into a binary system, a ternary system, and a more molecular system according to elemental composition. Common binary compound semiconductors are I-VI (such as Ag2Se, Cu2S, etc.), II-VI (such as CdSe, ZnS, etc.), III-V (such as GaAs, InAs, etc.), RMV family (such as SiC, GeSi, etc.), IV-VI (such as SnSe, PbS, etc.) and V-VI (Sb2Se3, Bi2S3, etc.). The ternary system and more elemental compound semiconductors mainly include I-III-VI (such as CuInSe2, AgInS2, etc.), I-II-IV-VI (such as Cu2ZnSnSe4, Cu2CdSnS4, etc.)
and some solid solutions (such as CdS, CuInxGaNxS2, etc.). Organic compound semiconductors are well known as naphthalene, anthracene, polyacrylonitrile, phthalocyanine, and some aromatic compounds. It can be seen from the classification of the above semiconductor materials that metal selenide plays a very important role in the entire semiconductor material family. The band gap width of selenide semiconductors is generally between 0.3 eV and 3.0 eV, covering a wide range from infrared to ultraviolet, so it has become a research focus in the semiconductor field and is widely used, such as solar cells, thermoelectric devices, illuminating and display. Devices, infrared detectors, lasers, nonlinear optical materials, hydrogen production by photolysis, and photocatalytic degradation.

2. Preparation process of germanide semiconductor material

Selenide bulk semiconductor refers to a solid material with a three-dimensional structure and a relatively large size. Due to its physical and chemical properties such as light, heat, electricity and magnetism, it also has the advantage of large size in the fields of optoelectronics, thermoelectricity and magnetic semiconductors. Has a certain application value. Selenide bulk semiconductors can be prepared by a variety of methods, including conventional melting, powder metallurgy, powder sintering, and sintering. Smelting is a traditional production process in which a solid raw material is melted into a liquid by a heating furnace and tempered, and the charging material undergoes certain physical and chemical changes at a high temperature to obtain a desired target product after cooling. The smelting method needs to be converted from liquid phase to solid phase, and the reaction process is affected by factors such as melting point, chemical activity, and saturated vapor pressure of each component. Therefore, for selenide semiconductors, vacuum melting and regional melting are widely used in practical applications. The vacuum melting firstly vacuum-packs the raw materials into the quartz tube and then puts them into the resistance furnace for high-temperature melting. Compared with the ordinary melting process, the advantages of vacuum melting are: 1 The raw materials are isolated from the external environment during the melting process, and the impurities can be ensured. To ensure the high purity of the product; 2 the evaporation of each component in the vacuum melting state is very small, and the segregation of components due to evaporation is greatly reduced, which is very important for Se having a high vapor pressure. 3 The vacuum melting process is simple in operation and short in production cycle, and has great application value in actual industrial production. Another regional melting technique (Zone Melting Technique) was first founded by Keek and Golay in 1953. In this method, only two parts of the raw material are melted at any time during the whole growth process, and the molten zone is supported by the surface tension, so it is also called "floating zone method". The raw materials used are generally first formed into sintered rods, and then the sintered rods are fixed by two chucks and placed vertically in the heat insulating tubes. The high frequency coil or focused infrared light is used to heat the portion of the sintered rod, and the melting zone is gradually moved from one end to the other end to complete the crystallization process. The crystal grown by this method has high quality and is often used for physical purification of materials, and also for growing crystals, especially single crystals. In recent years, with the rising research trend of selenide photoelectric and thermoelectric materials, reports on the preparation of high-quality selenide bulk semiconductors by the above-mentioned melting process are also emerging.

Powder metallurgy is the technical science of forming metal materials, semiconductor materials, composite materials, ceramic materials and their products by forming and sintering processes. At present, powder metallurgy technology has been widely used in transportation, machinery, electronics, aerospace, biology, new energy and information, and has become an important branch in the preparation of new materials. Powder metallurgy technology has a series of advantages such as remarkable energy saving, material saving, excellent performance, high product precision and good stability, which is very suitable for mass production. The general procedure for powder metallurgy is milling-press forming-sintering-post-treatment. Powder metallurgy is a commonly used and effective preparation process in the preparation of transition metal selenide semiconductor materials.

The conventional polycrystalline bulk semiconductor materials are basically cold pressed and then sintered. The bulk of the block obtained by this method has a low density, so that the mechanical
properties of the material are difficult to meet the processing requirements; The higher void ratio inside can significantly reduce the mobility of carriers, resulting in a large difference in the electrical conductivity of the material compared to the single crystal material. Later, researchers tried a variety of new forming or sintering processes, and the current progress is in the hot press sintering process. The hot press sintering refers to a method for preparing a material in which a dry powder is filled into a mold of a defined shape and heated while being pressed from a uniaxial direction to complete molding and sintering. It shows a typical vacuum hot-press sintering schematic and the corresponding heat treatment procedure. Hot pressure sintering has the following major advantages: When hot pressing, because the powder is in a thermoplastic state, the deformation resistance is small, easy plastic flow and densification, so the forming pressure is low; due to simultaneous heating and pressurization, it is beneficial to the powder. The mass transfer process such as contact, diffusion and flow of particles greatly reduces the sintering temperature and shortens the sintering time, which is also the most characteristic of hot press sintering. The hot press sintering is easy to obtain a sintered body close to the theoretical density, and the orientation effect of the crystal is easily realized. The obtained crystal grains are relatively small, and in general, a bulk material having good mechanical properties and electrical properties is easily obtained by hot press sintering. Hot press sintering has been extensively and deeply studied in the application of selenide bulk semiconductors. Here, the In4Se3 bulk thermoelectric material is taken as an example. The In4Se3 thermoelectric material is prepared by the combination of the smelting-pulverizing process and the hot pressing sintering. Shi et al first smelt-pulverize the raw material powder, and then sinter the prepared powder into a bulk In4Se3 at 450 °C. The maximum relative density of the material reaches 95.9%, and the sample has a value of 0.6 at 7000 °K. Later, in order to overcome the segregation of impurities caused by the smelting process, the powder was first mechanically alloyed, and the In4Se3 bulk thermoelectric material was prepared by hot pressing sintering during sintering. The sintering method can effectively avoid the volatilization of In and Se elements in the molten state. The utilization rate of the raw materials is improved, and the structure with uniform composition and fine particles is obtained, thereby improving the thermoelectric properties of the material. For example, Yang et al. reported that the high-purity In and Se were used as raw materials for mechanical alloying for one hour, and then hot pressed into a bulk of In4Se3 and the maximum ZT value of the sample was 0.93.

(4) Sparking Plasma Sintering (SPS) is a new technology for the preparation of bulk materials by sintering with a discharge plasma. Compared with the traditional sintering process, it has a heating sentence, a fast heating rate, and sintering. Low temperature, short sintering time, high production efficiency, fine and uniform product structure, high density materials, gradient materials and complex workpieces. Figure 1.2 is a schematic diagram of a typical SPS device, mainly composed of a pulsed DC generator, a vacuum system, a pressure system, a cooling system, and a control system. In recent years, research on the preparation of new materials by SPS at home and abroad has focused on ceramics, cermets, intermetallic compounds, composite materials and functional materials. Among the most studied are functional materials, including thermoelectric materials, magnetic materials, functionally graded materials, composite functional materials and nano-functional materials. Specific to the selenide semiconductor materials studied in this subject, the application of SPS to prepare selenide bulk semiconductors is becoming more and more extensive. Firstly, in the preparation of thermoelectric materials, Fu et al. used a combination of regional melting and SPS to prepare SnSe polycrystalline semiconductor thermoelectric materials with a ZT value higher than 1.0; Samanta et al. successfully prepared low thermal conductivity and high by vacuum melting combined with SPS. The thermoelectric properties of the n-type BiSe bulk semiconductor have a room temperature ZT value of 0.8 along the direction of the sintering pressure. The preparation of thermoelectric semiconductors by SPS is superior to the thermoelectric performance, and has the advantages of process, such as direct processing into wafers, without the need for cutting processing like unidirectional growth, which can effectively save materials and improve production efficiency. Wait. In the preparation of other selenide functional materials, SPS has also played an important role. For example, Wei et al. used ball milling and SPS to prepare high-density ZnSe bulk semiconductors, which provided a good foundation for subsequent
optical applications. Tyagi et al. reported the use of SPS to prepare Cu2Se photovoltaic materials. Maier et al. reported the use of ball milling combined with SPS to prepare a novel quaternary Ba2FePnSe5 (Pn=Sb, Bi) phase-change polycrystalline block.

3. Conclusion
As the core of modern high-tech, semiconductor technology has developed rapidly. New materials and various functional devices based on semiconductor technology have emerged in an endless stream, playing a vital role in all aspects of human life. Looking at the development of China's semiconductor industry, although it has maintained steady progress, there is still a big gap compared with the technological level of the world's major powers. The basis for the development of semiconductor technology is the development and application of semiconductor materials. Among a wide variety of semiconductor materials, selenide semiconductors are an important part of them, especially in the application of functional devices such as optics, optoelectronics, and thermoelectrics, and have important research significance. This thesis mainly studies the preparation and properties of Sb2Se3 and In2Se3W binary selenide semiconductors with excellent material properties but relatively weak research depth, and further explores the application of their optoelectronic functional devices.

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