Research progress in photoelectric materials of CuFeS$_2$

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Abstract. CuFeS$_2$ as a photoelectric material, there are many advantages, such as high optical absorption coefficient, direct gap semiconductor, thermal stability, no photo-recession effect and so on. Because of its low price, abundant reserves and non-toxic, CuFeS$_2$ has attracted extensive attention of scientists. Preparation method of thin film solar cells are included that Electrodeposition, sputtering, thermal evaporation, thermal spraying method, co-reduction method. In this paper, the development of CuFeS$_2$ thin films prepared by co-reduction method and co-reduction method is introduced. In this paper, the structure and development of solar cells, advantages of CuFeS$_2$ as solar cell material, the structure and photoelectric properties and magnetic properties of CuFeS$_2$, preparation process analysis of CuFeS$_2$ thin film, research and development of CuFeS$_2$ in solar cells is included herein. Finally, the development trend of CuFeS$_2$ optoelectronic materials is analyzed and further research directions are proposed.

1. Introduction

With the increasingly energy crisis and environmental pollution, the use of solar energy resources has become the focus of contemporary research, and solar cells are the most important form of solar energy utilization. Through the market survey found that 80% of people hope and willing to use solar energy as a new energy source[1-6]. Dating back to the development of solar cells, In 1839, the photovoltaic effect is discovered in dilute acid liquid for the first time by Alexander E. Becquerel. In 1905, German physicist Einstein's paper on the photovoltaic effect was published, and won the Nobel prize in physics in 1921. In 1949, W. Shockley, J. Bardeen, W. H. Brattain invented the transistor, and gave the p-n junction physical explanation, since then, semiconductor device era began. In 1954, The first practical monocrystalline silicon p-n junction solar cell which 4.5% efficiency have been discovered by D. M. Chapin, C. S. Fuller and G. L. Pearson in Bell laboratory in the United States. After several months, the efficiency reached 6% and reached 10% in a few years. Today, the total installed capacity of photovoltaic power generation in China is 43 million 180 thousand kilowatts, which has become the largest country in the global photovoltaic power generation capacity. Because of photovoltaic power generation is safe, reliable, pollution-free and rich in resources, solar cells have been applied to all aspects of life since human discovery and utilization of solar energy.

The structure of solar cell mainly consists of electrode, antireflection layer, window layer, buffer layer, absorbing layer, back electrode, substrate and so on. As the most important part of solar cells, the absorption layer has become the focus of research[7]. According to the difference of absorbing layer
materials, Solar cells are mainly divided into silicon solar cells, multi-comp-onent thin film solar cells, polymer multilayermodified electrode type solar cells and nanocrystalline photovoltaic solar cells.Compared with traditional silicon solar cells and GaAs,CdS,CdTe,CuInSe\textsubscript{2} thin film batteries,CuFeS\textsubscript{2} has the advantages of low price, abundant reserves and non-toxic.

2. background
Chalcopyrite compounds, such as CuAlS\textsubscript{2}, CuInS\textsubscript{2}, CuGaS\textsubscript{2}, CuInS\textsubscript{2} and CuFeS\textsubscript{2} have a wide band distribution, from 0.6eV-3.5eV, which belong to the three element sulfur group compounds.In recent years, CuFeS\textsubscript{2} thin films, nanowires, nanorods, spherical particles, nanocrystals in solar panels, thermoelectric devices and spintronic devices have attracted extensive attention of scientist. As a photoelectric material, CuFeS\textsubscript{2} is a ternary I–III–VI\textsubscript{2} group compound semiconductor, which has the structure of chalcopyrite and sphalerite\textsuperscript{[8]}. The crystal structure of CuFeS\textsubscript{2} is tetragonal, the lattice constant a=0.5289nm, c=1.0423nm, and its c/a constant is slightly changed by the material preparation process\textsuperscript{[9]}. CuFeS\textsubscript{2} is the only magnetic semiconductor material with ferromagnetic properties below 190K, and ferromagnetism between 190K and 823K. When TN is close to 823K, the structure of CuFeS\textsubscript{2} transforms from tetragonal chalcopyrite to cubic sphalerite, the copper and iron ions are disordered in tetragonal lattice. In the literature\textsuperscript{[10]}, the thermoelectric properties of CuFeS\textsubscript{2} doped with Co and Zn were compared with those of CuFeS\textsubscript{2} without doping any elements. The results show that the magnetic properties of CuFeS\textsubscript{2} can be changed by doping, which affects the thermoelectric properties of CuFeS\textsubscript{2}.

CuFeS\textsubscript{2} is a direct band gap semiconductor material with a band gap of 0.6eV and a high optical absorption coefficient\textsuperscript{[11]}, which is very useful for broadening the absorption range and reducing the loss of carrier. The structure morphology, crystallinity, crystal defects, grain boundaries and elemental components have great influence on the optical properties of CuFeS\textsubscript{2}. Literature research shows that the composition of the material and the stoichiometric deviation of the smaller, the more regular morphology, crystal defects, the better the optical absorption characteristics. The absorption characteristics of CuFeS\textsubscript{2} thin films with a single chalcopyrite structure better than non single structure. The band gap of CuFeS\textsubscript{2} is mainly affected by the change of crystal lattice parameters and the change of structure\textsuperscript{[12-13]}. The electrical properties of CuFeS\textsubscript{2} are determined by inherent defects, impurities and grain boundaries in the films. CuFeS\textsubscript{2} exists as a n-type system due to the narrow band, and it is formed heterojunction solar cells with wide band system resin\textsuperscript{[14]}. In 1917, the structure of CuFeS\textsubscript{2} was studied by Burdick and Ellis, indicating that the structure of chalcopyrite is similar to that of sphalerite structure, that is, cuprous ion and iron ion in chalcoprite structure are correspond to two zinc ions in phalerite structure\textsuperscript{[15]}. In 1987, CuFeS\textsubscript{2} as cathode materials for lithium batteries was studied by Fong and Eda, it was found that Li/CuFeS\textsubscript{2} battery forming a discharge platform in 1.5V at room temperature\textsuperscript{[16]}. In 2011, CuFeS\textsubscript{2} as cathode materials for lithium batteries was studied by Ding Wei. After studying the discharge at room temperature, it was found that there are two discharge platforms at 1.75V and 1.5V\textsuperscript{[17]}. In 2014, CuFeS\textsubscript{2} nanoparticles was prepared by Zhang Zhuolei with high temperature oil phase thermal injection method, the test results show that CuFeS\textsubscript{2} nanoparticles have a certain photoelectric response ability.

To produce a high-efficiency CuFeS\textsubscript{2} solar cells, the key is to obtain the maximum short-circuit current and the maximum open circuit voltage\textsuperscript{[18]}. On the one hand, it is necessary to increase the absorption coefficient of light. In the literature\textsuperscript{[10]}, changed the magnetic properties of CuFeS\textsubscript{2} by doping appropriate amount of Co, thereby the thermoelectric merit ZT of CuFeS\textsubscript{2} is changed to improve the absorption coefficient of light. The study shows that the energy band of nanoparticles chalcopyrite is 1.2eV, and the energy band of bulk chalcopyrite is 0.6eV. Therefore, the power factor of nanoparticles chalcopyrite is higher than that of bulk chalcopyrite, the thermal conductivity decreases greatly, and the efficiency increases by 77 times\textsuperscript{[19]}. On the other hand, it is necessary to reduce the recombination current as much as possible, reducing the concentration of defect states in the material can effectively reduce the recombination of photogenerated carriers\textsuperscript{[20-23]}. It is necessary to find the appropriate preparation method to reduce the defects in the material and obtain uniform morphology to reduce the surface recombination.
3. methods
Preparation method of thin film solar cells are included that Electrodeposition, sputtering, thermal evaporation, thermal spraying method, co-reduction method. Electrodeposition is a commonly used method for preparing semiconductor thin film materials. It has high controllability, simple process, less investment, environmental protection and economy, suitable for commercial operation, no requirement for deposition matrix structure, but with low degree of crystallization and deficit hyperactivity. At present, the preparation of CuFeS$_2$ photoelectric film by electrodeposition has not been reported. Sputtering method means that in the vacuum, the target surface is hit by high energy particles, the atoms or molecules in the target are ejected and deposited on the substrate. It has good adhesion with the substrate, thin film material can be controlled, suitable for large area production, process parameters, easy to control, but the sputtering needs harsh conditions, expensive equipment and high cost. Practice has proved that the sputtering method is not suitable for CuFeS$_2$ photoelectric film preparation. Thermal evaporation method means that putting the raw materials of high purity into the vacuum conditions of container, it makes the sublimation and evaporation deposition onto the surface of the substrate specific. The co-reduction method is a recently popular method for the preparation of solar cells, which is mainly a method of occurring the reduction reaction under a certain temperature and pressure. Compared with other methods, it has many advantages. Firstly, it can directly get good crystalline powder and is no need for high temperature ignition to avoid the agglomeration of powders which may be formed during the burning process. Secondly, powder crystal phase and morphology related to hydrothermal reaction conditions. Finally, the preparation process is relatively simple, low cost. At present, the most common method for preparing CuFeS$_2$ photoelectric film is the co-reduction method. In 1999, Hu Junqing prepared CuFeS$_2$ nanorods with photoelectric properties by co-reduction method, which materials such as CuCl$_2$, FeCl$_2$, 6H$_2$O, (NH$_4$)$_2$S$^{[27]}$. In 2013, Igor S. Lyubutin prepared self-organized single-crystalline nanobricks of chalcopyrite CuFeS$_2$ by co-reduction method, which materials such as (Cu(COOCH$_3$)$_2$, H$_2$O), (Fe(COOCH$_3$)$_2$)$^{[19]}$. In 2016, K.M. Deen, E. Asselin prepared CuFeS$_2$ nanopowders by co-reduction method, which materials such as (CuCl$_2$, 2H$_2$O), (FeCl$_2$, 4H$_2$O), (CS(NH$_2$)$_2$)$^{[15]}$.

4. Summary
CuFeS$_2$ has excellent photoelectric and magnetic properties as a solar cell material. This paper mainly introduces the structure of solar cell and the development of solar cell at domestic and foreign, as a solar thin film cell, CuFeS$_2$ has high optical absorption coefficient, and is a direct gap semiconductor with good thermal stability and no light fading effect. Recent studies have shown that CuFeS$_2$ has the photoelectric response ability in solar cells, and can be used as thin film solar cells. In this paper, the preparation technology of CuFeS$_2$ solar thin film and the research progress of various preparation processes are introduced. Finally, the development trend of CuFeS$_2$ photoelectric materials is analyzed and further research directions are proposed. Chalcopyrite CuFeS$_2$ is abundant in nature, cheap and non-toxic. If it can be widely used in solar cells, which will completely solve the human energy problems. So CuFeS$_2$ thin film battery will certainly go to people's line of sight. It's very important for us to adopt new methods and new technologies.

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