

Photoelectric Material CuInSe_2 *

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Abstract: This paper gives a review of CuInSe_2 solar cells techniques and recent developments in CuInSe_2 materials, it is reported that solar cells based on CuInSe_2 have demonstrated efficiency of 18%. It also introduces the characteristics of CuInSe_2 : the extraordinarily high absorption coefficient ($> 10^5 \text{ cm}^{-1}$), the use of thin layers ($1 \sim 2 \mu\text{m}$), long-term stability. The understanding of CuInSe_2 will be helpful to the research of thin-film solar cells with high conversion efficiency both at home and abroad.

Key words: photoelectric material; CuInSe_2 ; solar cell

CLC number: TG146, TK513.1

Document code: A

Article ID: 0529-6579(2003)S1-0035-03

1 Introduction

Exploit new energy and regenerable energy is one of the most decisive fields of technology in world's development, it is also an important way to solve problems of energy and environment. In 1954, the first modern solar cell was developed in Bel Lab, laid a foundation for using solar cells in large scale. For decades, especially after the 1970's oil crisis, environmental pollution and the advantages of solar cells, such as: large in quantity, safety, no moving parts, no air and water pollution, require little maintenance etc., make solar cells develop rapidly.

The mechanism that makes solar cells work is photoelectric effect. In 1876, scientists found the first solid material which possesses photoelectric effect-Se, showed that semiconductors are the most suitable materials for energy conversion between photo and electricity^[1].

Silicon is indirect energy gap semiconductor, it has low absorption coefficient, in turn its films are thick and large. Though commercial silicon solar cells are comparatively simple, the needed purity of raw material is low, but efficiency and stability are the problems which needed solve. Additionally, silicon used in solar cells mostly come from substandard product of semi-conductive silicon. So it can not satisfy with the need of photovoltaics.

Binary compounds, such as: GaAs, CdS, CdTe, InP etc., have high absorption coefficient, so are suited to prepare films of several microns, and can reach high conversion efficiency. But GaAs is very expensive and As is poisonous. To prepare binary compounds thin-films

need sophisticated equipment, large funds and long period of time. So they do not suit to large scales produce.

Ternary compounds provide vast vistas for choosing photoelectric materials. Chalcopyrite compounds are becoming important solar cell materials, for their excellent performances, cheaply technology. CuInSe_2 is one of the most promising materials, its band gap is about 1.04 eV which is within the maximum solar absorption region. This is very important as far as the optimum conversion efficiency is concerned. The direct energy gap of CuInSe_2 results in a large optical absorption coefficient ($> 10^5 \text{ cm}^{-1}$), which in turn, permits the use of thin layers ($1 \sim 2 \mu\text{m}$) of active material. CuInSe_2 -based solar cells have shown efficiency of 18%^[2], $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ -based solar cells have reached 18.8% of efficiency^[3]. CuInSe_2 solar cells are also known for their long-term stability.

The problems we faced are to find an advanced technology to reduce production costs, raise efficiency and prepare CuInSe_2 in large scale. This paper reviews the research of CuInSe_2 solar cells history, current situation, character, existing problems and trend of development.

2 Present situation of CuInSe_2 solar cells

Since Bel Lab developed single-crystal CuInSe_2 in 1974, conversion efficiency of CuInSe_2 has been raised rapidly, as showed in Fig.1, and the cost of CuInSe_2 is increasingly reduced.

In 1976, Maine University first developed CuInSe_2 solar cells, which reached 6.6% of efficiency.

In 1982, Boeing Company developed CuInSe_2 solar

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cell by evaporating Se, Cu, In, its efficiency was over 10%.

In 1983, Arco Solar Company put forward a new technology-selenization. The technology is simple, low cost, and is one of the most important techniques for preparing CuInSe₂ solar cells.

In 1988, Arco Solar Company developed CuInSe₂ solar cell which showed conversion efficiency of 11.1%, exceeded 10% of efficiency for the first time and showed long-term stability.

In 1994, Sweden Royal Institute of Technology reported 17.6% of efficiency in area of 0.4 cm², set a word record of CuInSe₂ solar cells, marked CuInSe₂ solar cells good prospects for industrialization development.

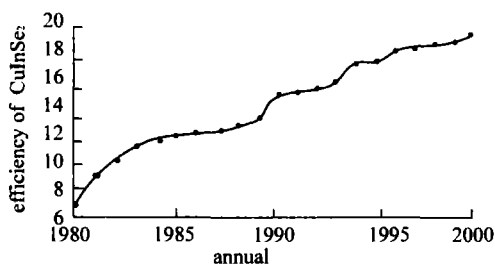


Fig.1 The efficiency of thin film solar cells CIS varies annually

Contreras and Shock developed CuIn_{1-x}Ga_xSe₂ solar cells reached 18.8% of efficiency in the year of 1999 and 2000 respectively, by using multi-vacuum technology.

Several research groups have prepared devices-quality CuInSe₂ or CuIn_{1-x}Ga_xSe₂ by using either one-step or multistep processes^[4]. In the one-step process, the CuInSe₂ or CuIn_{1-x}Ga_xSe₂ thin-film is grown by codeposition of Cu, In(Ga) and Se simultaneously. The techniques used for one-step processes are physical evaporation, chemical deposition and electrodeposition. The multistep process involves, for example, the deposition of precursor films of In(Ga)-Se in the first step, Cu-Se in the second step, and again deposition of In(Ga)-Se in the final stage. To date, the techniques used for multistep processes are physical evaporation and sputtering.

3 Structure of CuInSe₂

CuInSe₂ belongs to I - III - VI₂ compounds, it is a derivation of II - V compounds.

The elements of II are substituted by Cu and In, thus forms ternary compound semiconductor. CuInSe₂ has two allotropic substances: chalcopyrite and blende. When temperature is above 980 °C, it is blende structure; when the temperature is below 810 °C, it belongs to

chalcopyrite structure, as shown in Fig. 2. Chalcopyrite CuInSe₂ is excellent match with CdS, this make it superior to the other chalcopyrite alloys.

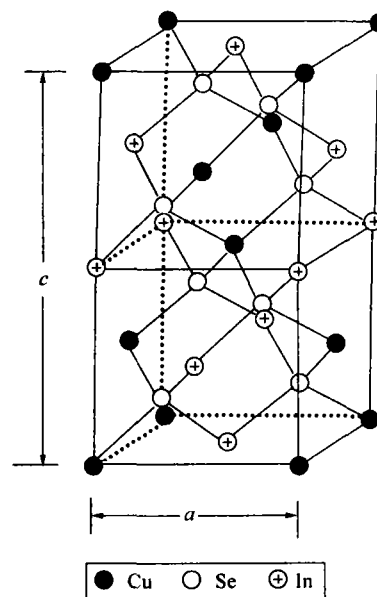


Fig.2 Chalcopyrite CIS

From the phase graph of CuInSe₂, we can see when ratio of composition elements deviate from Cu:In:Se = 1:1:2 to a certain degree, the materials still have chalcopyrite structure and the same physical and chemical characters. Because I - III - VI₂ compounds have twelve kinds of intrinsic point defect, and these point defect can create new energy band in band-gap. Meanwhile, CuInSe₂ can be prepared either *p*-type or *n*-type semiconductors, by adjusting ratio of composition elements, not by including other elements.

4 Character of CuInSe₂

CuInSe₂ band-gap is about 1.04 eV at room temperature, the most suitable band-gap to absorb sun shine is about 1.45 eV. So scientists include other elements in CuInSe₂ to raise the efficiency of CuInSe₂. Researchers mainly use Ga substitute In, S substitute Se. In fact control content of Ga and S will influence the ratio of Cu/In. Include Ga and S also influence crystal size and lattice defect, so the efficiency is not the highest when band-gap nears 1.45 eV. At large, include Ga can raise open-circuit voltage, lower the short-circuit current. Now CuIn_{1-x}Ga_xSe₂ solar cells have reached 18.8% of efficiency, it is the highest efficiency reported.

CuInSe₂ is direct-band semiconductor, its absorption coefficient is high (> 10⁵ cm⁻¹), and the absorption spectrum of CuInSe₂ is large, showed in graph(3)^[5].

5 Prospect of CuInSe₂

The importance of CuInSe₂-based solar cell for photovoltaic system has been recognized for thirty years. In the last decade, the cells' efficiency has rapidly progressed by understanding the CuInSe₂ film formation, the role of Na and solid solution of Ga and S etc. CuInSe₂ solar cells continue to advance with an efficiency of exceeding 18%.

Although CuInSe₂ is a promising material, it has many limitations. It is no doubt that CuInSe₂ is long-term stability, high efficiency, but the cost is a problem which needs to be solved, because of the cost of In and the process. In is the most expensive element in CuInSe₂, we can overcome it by preparing thinner film, retrieving In

and using other elements to substitute In.

So, the understanding of CuInSe₂ will be helpful to the research of thin-film solar cells with high conversion efficiency.

Acknowledgement: This project is supported by Jiangxi Provincial Natural Science Foundation of China

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光电材料 CuInSe₂ 薄膜

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摘 要: 概述了 CuInSe₂ 太阳能电池技术, CuInSe₂ 材料的最新发展; 同时也介绍了 CuInSe₂ 薄膜的特性: 非常高的光吸收系数 ($> 10^5 \text{ cm}^{-1}$), 可以将薄膜做的很薄 ($1 \sim 2 \mu\text{m}$), 长期的稳定性, 抗辐射性等。对 CuInSe₂ 材料的认识、了解将有助于对高效、低成本的薄膜太阳能电池的研究。

关键词: 光电材料; CuInSe₂; 太阳能电池

中图分类号: TC146, TK513.3 **文献标识码:** A