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博　士　学　位　论　文

铜铟镓硒薄膜太阳电池的模拟与工艺优化

Simulation and Process Optimization Research of CuInGaSe_2 Thin Film Solar Cells

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摘 要

人类对能源消费的不断增加，传统化石能源的快速消耗导致环境恶化加剧，雾霾等恶劣气候频发，严重影响人类的身体健康和生存，寻找可再生清洁能源成为全球共同追求的目标。太阳能是一种可持续的清洁能源，受到科学家的热衷追捧，而光伏产业作为无污染的新能源产业获得世界各国青睐而得到广泛应用。

以中国光伏产业为代表的发展中国家，其新能源产业以前所未有的速度发展，对世界新能源产业做出巨大贡献，但是由于发达国家的贸易“双反”政策及国内市场开发不足导致以晶硅为主的中国光伏产业遇冷，而薄膜太阳电池却未受到双反的限制。铜铟镓硒（CIGS）薄膜电池是一种高效率、超廉价的薄膜电池，它的研究受到世界各国研究者的重视，同时由于CIGS薄膜电池具有其稳定性高、可制备柔性电池等优点，实现商业化的价值更高，未来CIGS薄膜电池的产业将直接占领一部分光伏市场。

实现CIGS薄膜电池的广泛应用必须制备出这种高效率的电池，且同时降低其制备成本。当前CIGS薄膜电池的制备方法主要有溅射后硒化、共蒸发及非真空印刷等几种方法，共蒸发和溅射法制备技术的价格较为昂贵，采用非真空法制备CIGS薄膜电池是降低其制备成本的主要路径，而优化CIGS电池的制备工艺是实现低成本和高效率电池的主要手段，因此本文采用数值模拟的研究方法和部分工艺优化的方法实现对电池效率提升和成本的有效降低。

本文主要开展三个方面的研究，一、采用wxAMPS软件进行数值模拟进行优化研究；二、探索采用非真空方法来制备CIGS薄膜材料；三、研究掺Na的Mo薄膜电极特性，研究MoNa电极对CIGS薄膜电池性能的主要影响，其结论如下：

1、通过采用wxAMPS模拟软件进行参数设计，研究各种不同影响因数条件包括各层膜厚度、载流子浓度、缺陷浓度、温度及不同禁带宽度组合方式等对CIGS薄膜电池的开路电压（Voc）、短路电流（Isc）、填充因子（FF）及效率（Eff）造成的影响。理论上得到的高效率的CIGS薄膜电池最佳的优化条件为CIGS厚度3μm，CdS厚度30nm，ZnO厚度100nm，为制备高效率薄膜太阳能电池提供

了理论基础。同时理论研究了超薄 CIGS 薄膜制备的设计，提出制备高效超薄 CIGS 薄膜电池的可能性。

2、采用非真空刮涂法制备 CIGS 薄膜材料，通过优化各种无机盐配比，得出一种最佳配比。采用不同空气氧化退火条件，硫化退火温度条件及硒化退火条件，研究结果实现 CIGS 薄膜最佳退火条件选择为：空气退火温度为 400℃、硫化温度为 500℃、硒化温度为 500℃。采用通氢热处理后充分硫化和硒化后可以获得 P-型，结构较完整的 $CuInGaSe_2$ 材料，其迁移率约为 23..17 $cm^2/V\cdot s$，空穴浓度约为 $4.5x10^{15}cm^{-3}$，达到作为 CIGS 太阳电池的吸收层要求

3、通过空气加热氧化后的金属氧化物进行氢化还原成金属合金，氢化温度条件为 400℃，氢化时间为 30min，氢化之后金属合金硒化所形成的 CIGS 薄膜质量得到较大提高，探索低温等离子氢化，研究表明等离子氢化具有一定程度改善薄膜质量的作用。

4、对掺 Na 钼薄膜电极进行优化研究，纯 MoNa 薄膜电极氧化特别严重，电阻率也较大。采用多层 Mo/MoNa/Mo 薄膜组合方式，制备的 MoNa 薄膜电极较低电阻率为 $4.62\times10^{-4}\ \Omega\cdot cm$，其对应 MoNa 薄膜厚度为 100nm，同时研究了不同 MoNa 薄膜厚度对 CIGS 薄膜产生影响，一定厚度 MoNa 薄膜电极对 CIGS 薄膜具有质量改善作用。

5、制备了 CdS 缓冲层、ZnO 窗口层及导电薄膜层 ZnO：Al，并研究了其相关的特性，表明 CdS、ZnO 及 ZnO：Al 具有较好光学特性。通过在不同厚度 MoNa 薄膜电极上制备 CIGS 薄膜电池，研究其相应电性能，结果表明在 100nm 厚度的 MoNa 薄膜上制备的 CIGS 薄膜电池具有较高效率，其平均效率为 6.85%，是所有 MoNa 薄膜中实现效率最高的电池。

关键词：CIGS 薄膜电池；数值模拟；非真空；MoNa 薄膜电极；电性能

Abstract

Energy consumption for human society has been accelerated and the large exhaustion of traditional fossil fuels has led to the deterioration of the environment, forming severe climatic such as fog haze, which seriously influences human health and survival. It is becoming a global common goal to find the sustainable renewable and clean energy. As a kind of sustainable and clean energy, solar energy is well received by scientists. Photovoltaic is widely used around the world as a pollution-free and new energy.

As a developing country, Chinese photovoltaic industry is developing at an unprecedented speed, which has a great contribution to the world's new energy industry. Because of the dual anti-dumping and anti-bribery policy for developed countries and weak driving force on domestic market for China, at present the crystalline silicon photovoltaic industry encounters winter season in China, but there is no effect on thin film solar cells. As one of the highest efficiency thin-film solar cells, Copper indium gallium selenium (CIGS) thin-film cells are also researched by researchers around the world, and at the same time because of the advantages of the CIGS thin film cells, such as the high stability and the flexible cells preparation , its commercial value is higher than other cells. In the future CIGS cells industry may get a rapid development and will occupy a part of the market.

CIGS thin-film cells which depend on the high efficiency and low fabrication cost are widely used. Currently, preparation methods of CIGS solar cells are mainly including thermal evaporation、selenization after sputtering and the non-vacuum printing, etc. Because of high cost for thermal evaporation and sputtering technology, the main way for low cost is to adopt non-vacuum preparation method of CIGS thin film cells, and the primary way to realize the goal of low cost and high efficiency is to optimize preparation process. We use numerical simulation methods and process optimization to improve the efficiency and reduce the cost in this paper.

In this paper there are three aspects for research work: first, use wxAMPS software to do numerical simulation research. Second, explore the non-vacuum preparation methods of CIGS thin-film material. Third, study on the characteristics of Na-doped Mo thin film electrode and the impacts of CIGS thin-film cells performance.

The main conclusions are as follows:

1. With wxAMPS simulation software, performances of CIGS thin-film cells, such as open circuit voltage (Voc), short circuit current (Isc), fill factor (FF) and efficiency (Eff), are effected by the conditions of various influence factors including the thicknesses of each thin-film layer, carrier concentration, defect concentration, temperature and forbidden band width of the different combinations, etc. In theory, optimization conditions for the highest efficiency CIGS cells are 3μm CIGS thickness, 30 nm CdS thickness and 100 nm ZnO thickness. It provides theoretical basis for the preparation of high efficiency thin film solar cells. At the same time, it proposes the theoretical study of ultra-thin CIGS thin film preparation, and the high efficiency of ultra-thin cells has been got.

2. Use non-vacuum coating method to prepare CIGS thin film material. Choose the best proportion by optimizing the ratio of various inorganic salt. Employing different air oxidation annealing conditions, different sulfide annealing temperature conditions and different selenide annealing temperature conditions, the optimization conditions for best CIGS thin film preparation are as follows, 400℃ air annealing, 500℃ sulfide annealing, 500℃ selenide annealing. Using sulfide and selenide after hydrogenation, P-type $CuInGaSe_2$ thin films have the full structure. As CIGS solar cell absorber layer, the mobility and the hole concentration which meet the requirements, are respectively about 23.17 $cm^2/V\cdot s$ and $4.5\times10^{15}cm^{-3}$.

3. Employ hydrogenation reduction, metal oxides which is prepared though air heating oxidation is restored to become metal alloy. Hydrogenated temperature is 400 ℃, and hydrogenated time is 30 min. Metal alloy after hydrogenation is becoming CIGS thin film with selenium, and quality of thin film is improved greatly. Exploring low temperature plasma hydrogenation, the results have shown that the quality of thin film can be greatly improved by plasma hydrogenation.

4. The optimization of Na-Doped Mo thin film electrode was researched. Pure MoNa thin film electrode is seriously oxidized, and the resistivity is high. Use the combination of multilayer Mo/MoNa/Mo film, the corresponding resistivity of 100 nm MoNa thin film electrode is only $4.62\times10^{-4}\ \Omega\cdot cm$. The CIGS thin films which prepared on MoNa thin film of different thicknesses were studied. The quality of CIGS thin film can be improved under a certain thickness MoNa thin film.

5. CdS buffer layer, ZnO window layer and ZnO: Al conductive film layer were

prepared, and it indicates that all the above layers have good optical properties. CIGS thin film cells prepared on different thickness MoNa thin film electrode were studied, and the results show that CIGS thin film prepared upon the 100 nm thickness MoNa film has the highest efficiency and the average efficiency reaches 6.85%.

Keywords： CIGS thin film cell; numerical simulation; non-vacuum; MoNa thin film electrode; electrical performance

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