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Executive Summary

Developing CIGS solar cells calls for the understanding of materials and processing in order to translate the record small efficiency to module and the strategy to produce thin cells for materials and processing saving.

This project has exploited nanostructuring of CIGS solar cells, including nanowires and nanotextured substrates. We showed that nanowires function as well-defined CIGS-CdS p-n junction for understanding the chemical fluctuation, defect formation interface and grain boundary behaviors and the effect of ion diffusion, which are important but complicated issues for solar cell fabrication. We have also demonstrated effective nanoscale photon management on nanotextured substrate to provide opportunity for thin CIGS solar cells. We also developed the scalable methods for producing such nanotextured substrates. The research output in this project helps advancing the CIGS solar cells and broadly other solar cell technologies in cost reduction per unit power.

Introduction

The existing thin film CuIn(Ga)Se₂ (CIGS) solar cells reach ~20% power efficiency in research labs while the large module efficiency was ~12%. CIGS solar cell is a promising technology for future generation photovoltaic devices. A typical CIGS solar cell consists of Mo contact, 1-2.5 mm absorber layers (CIGS), pn junction formed by CIGS and CdS, 50 nm buffer layer (CdS), and window layer (heavily doped ZnO). However, large-scale deployment of CIGS solar cells requires new characterization, materials, and processes to further increase the solar cell efficiency at the modules and reduce the cost. The following research opportunities exist: 1) Absorption of sunlight within thinner CIGS absorber layer. Developing a light trapping device structure is an approach to reduce the amount of absorber materials. Using thinner absorber layers is important since the availability and price of In might be an issue for large scale deployment. 2) The CIGS/CdS materials and junction are highly complex and require further understanding of chemical inhomogeneity and defect properties. It also requires the understanding how processing affect the structure and property. These understandings will help bring up the module efficiency.

Research Approach

This project exploits nanostructuring in CIGS solar cells, which offer many advantages to enable better thin film cells. The nanostructuring methods include nanowires (NWs) and nanotextured substrates. First, we explore NWs as well-defined CIGS-CdS p-n junction interface to separate electrons and holes and there are no free CIGS surfaces, which can decrease the recombination loss. NWs are well-defined nanoscale domains for studying the chemical fluctuation, defect formation interface and grain boundary behaviors and the effect of Na⁺ ions, which are important but complicated issues for solar cell fabrication. Second, NWs and nanotextured substrate provide opportunity to use the knowledge learned from nanoscale photonics to perform light trapping to enhance absorption with small amount of materials, which is important due to the price and availability of In. With the existing knowledge on CIGS materials and the issues identified, the goal of this project is to provide better understanding the CIGS materials and interfaces and to enable thin cells for low-cost.

Research Results and Significance

Synthesis of CIGS-related NWs

We have successfully synthesized NWs with a variety of compositions. We exploited the vapor-liquid-solid (VLS) process for the growth of NWs. We used a tube-furnace synthesis apparatus for NW growth. For example, CuInSe₂ NWs. NWs were grown on substrates with Au nanocrystals or annealed Au film as catalysts. The substrates were placed downstream in a horizontal tube furnace with the CuInSe₂ source material heated at the center. The position of substrate is important since the temperature changes with position. Since the targeted CIGS NWs require complex four-element process, we have conducted a serial of NW synthesis from binary to quaternary system to study the evolution of materials synthesis and structure. So far we have been successful in the synthesis of In₂Se₃, GaSe, In₂Ga_{2-x}Se₃, and CuInSe₂ NWs. Fig. 1 shows a SEM image from these NWs. They are randomly oriented and have diameter around 20-200 nm and length up to tens of micrometers and can be controlled. The size of NWs are ideal for our NW solar cell device concept.

Fig. 1 Scanning electron micrograph of CuInSe₂ NWs.

However, we also found that the growth yield of CuInSe₂ NWs is not very high, which is due to the low Cu vapor pressure during CuInSe₂ evaporation. Although we can use additional Cu source such as CuI₂, controlling Cu vapor pressure is not easy. Therefore, We have designed a new strategy (Fig. 2) in producing high yield of CuInSe₂ NWs by using In₂Se₃ NWs as template to react with copper metal directly. Since In₂Se₃ NWs can be made with very high yield, it is now possible to obtain high yield of CuInSe₂ NWs. We found very exciting phenomena when chemically transforming In₂Se₃ into CuInSe₂ NWs. First, the transformation is epitaxial. That is, single-crystalline CuInSe₂ NWs have been produced with single-crystalline In₂Se₃ NW templates. Second, we have found the high anisotropy of transformation temperature for different growth directions of In₂Se₃ NWs. The [0001] direction NWs were found to have a very low transformational temperature (below 350 °C) while the [11-20] NWs did not transform until 580 °C. This transformation anisotropy is due to the bonding and shape anisotropy of NWs. Our results might have important implications to the thin film CIGS processing as well.

Fig. 2 a) Schematic of the test structure, and the proposed chemical reaction leading to the transformation. b) View of the In-Se layers in the IS

crystal structure. Red atoms are Se, grey are Cu. c) View of the plane similar to that shown in b) for the CIS crystal structure, with orange Cu atoms. d) [10-10] projection of the IS structure showing the ABAB stacking sequence of the Se anion sublattice. e) [1-10] projection of the CIS crystal structure showing the ABCABC stacking sequence of the anion sublattice.

Studying CIGS structure evolution during processing

The structure of CIGS materials can change with processing is an important factor affecting the solar cell behavior. NW solar cell fabrication process includes synthesis of NWs, chemical bath deposition of CdS, sputtering of ZnO etc. The chemical composition can change during solar cell device fabrication due to heating and/or coating another layer of materials. To study the structure and composition, we have used transmission electron microscopy (TEM) with atomic resolution and selected area electron diffraction (SAED) and exploit the analytic tools associated with TEM such as energy dispersive X-ray spectrometry (EDX) with sub-1 nm resolution. We have found very interesting results. First, vacancy ordering was found In₂Se₃, In₂Ga_{2-x}Se₃, and CuInSe₂. We observed superlattice formation due to vacancy ordering. We believe that this can affect electronic structure and is important for solar cell behaviors. Second, Cu ions were found to be very mobile in CuInSe₂ NWs. During chemical bath deposition of CdS, Cu ions can diffuse out to form superlattice structure and eventually produce hollow nanotubes (Fig. 3). This observation is very important for understanding the solar cell fabrication process.

Fig. 3 TEM images of CIS-CdS structure with chemical deposition time of 12 (top) and 16 min (bottom), showing voids and nanotube formation, respectively.

Electrical property by single NW transport measurement

We have developed single NW electrical measurement technique. We found very large anisotropy of electrical conduction in In₂Se₃ NW. Layer-structured indium selenide (In₂Se₃) nanowires (NWs) have large anisotropy in both shape and bonding. In₂Se₃ NWs show two types of grow directions: [11-20] along the layers and [0001] perpendicular to the layers. We have developed a powerful technique combining high-resolution transmission electron microscopy (HRTEM) investigation with single NW electrical transport measurement, which allows us to correlate directly the electrical properties and structure of the same individual NWs. The NW devices were made directly on a 50-nm-thick SiN_x membrane TEM window for electrical measurements and HRTEM study. NWs with the [11-20] growth direction exhibit metallic

behavior while the NWs grown along the [0001] direction show n-type semiconductive behavior. Excitingly, the conductance anisotropy reaches $10^3 - 10^6$ at room temperature, which is 1 – 3 orders magnitude higher than the bulk ratio.

Fig. 4 Scheme of an in-situ TEM devices and the transport properties for the two growth directions.

Fig. 5 a) Resistivity and b) mobility of CIS nanowires as a function of diameter

Figure 5 shows the results of electrical transport measurements on single CuInSe₂ NWs as a function of NW diameter. Blue points were taken from NWs with a linear IV behavior, while red points were from NWs with nonlinear IV behavior. Several, but not all, of the resistance values were measured with 2 and 4 point measurements, in all measured cases contact resistance was less than 10% of the total resistance measured. Mobility data were extracted from measuring the gate dependence of the resistance, and all NWs showed p-type conduction. Generally the NWs are more resistive (between 10 and 1000 Ω cm) and have lower mobilities (between 10^{-2} and 10^{-4} cm²/s) than would be expected of p-type CIS, which is normally reported to have a resistivity of ~ 0.001 Ω cm, and a mobility of 50-150 cm²/s. The carrier density calculated from these numbers is between 10^{18} and 10^{20} /cm³, which is higher than the typical value of 10^{16} used in CIS solar cells. The most striking feature of the plots is the dramatic increase in resistivity and decrease in mobility which is observed as the NW diameter approaches 90 nm. The resistance and mobility were calculated assuming the entire NW has uniform conductivity. If we instead assume that there is a 40 nm region on the circumference of the NW which is highly resistive, possibly due to an accumulation or organization of charged defect species at the free surface, a relatively uniform resistivity of 1 Ω cm can be calculated for all NWs. In this case the reported mobilities can be seen as an absolute lower bound, but the actual mobilities may be perhaps an order of magnitude higher. The mobility expected under this hypothesis would unfortunately depend sensitively on the geometry of the conducting channel, which is currently unknown. These results emphasize the immense importance of interfaces to electrical transport in this materials system.

Photon management on nanotextured substrate

Fig. 6 Nanodome amorphous Si solar cell structure, which will be modified to be applied to CIGS. SEM taken at 45 degree on a) nanocone quartz substrate b) a-Si:H nanodome solar cells after deposition of multilayers of materials on nanocones. Scale bar 500 nm.

We have used amorphous Si nanocone and nanodome solar cells as a model system to study the light trapping since they are easily deposited within our current facility. We have also applied this understanding to CIGS. The nanodome solar cells, which have periodic nanoscale modulation for all the layers from the bottom substrate, active absorber to top transparent contact. These devices combine many nanophotonic effects to achieve both efficient antireflection and absorption enhancement over a broad band of spectra. Nanodome solar cells of hydrogenated amorphous silicon (a-Si:H) with only 280 nm thick layer can absorb 94% of light with wavelengths of 400 to 800 nm, significantly higher than 65% of flat film devices. Because of near complete absorption, the large short circuit current of 17.5 mA/cm² in nanodome devices exceeds that in the world record single junction a-Si:H solar cells. Excitingly, the light management effects remain efficient in a wide range of angles of incidence, favorable in the real environment with significant diffuse sunlight. We demonstrate nanodome devices with a power efficiency of 10.8%. The nanodome structure is not limited to any specific material and we have been applying to CIGS solar cells. We showed that a thin layer of CIGS can absorb all the light and enhanced charge carrier collection.

Rolling process for nanostructured substrate

We have developed a rolling process to produce large-scale nanotexturing on a variety of substrate surface, which can be used to fabricate CIGS nanostructured solar cells. Fig. 7 shows the rolling process to fabricate such a substrate. Fig. 8 shows the nanoparticle substrates can be produced with excellent control.

Fig. 7 Rod coating process to produce large area nanocone substrate.

Fig. 8 Rod coating process to produce close-packed nanoparticles on substrate ranging from mono-, double- to multiple layers of particles.

We also developed another method of nanoscale texturing to create the right sizes for CIGS materials. This method involves in controlling oxidation of low melting melts and generates nanocone morphology. We have deposited CIGS onto our nanotextured substrate. We have developed nanowell substrates. We have compared different shapes of nanotexturing for mimicking nanowire-like solar cells. We have seen improved photon management effect.

Comparison of research accomplishments with project

- Task 1. Synthesis of NWs (Accomplished)
- Task 2. Correlate structure with properties (Accomplished)
- Task 3. Single core-shell NW solar cells (Accomplished)
- Task 4. Ensemble solar cell processing and testing (Accomplished)
- Task 5. Further NW materials development (Accomplished)
- Task 6. Roll-to-Roll process (Accomplished)

Conclusions and Opportunities for future work

We have exploited nanostructuring of CIGS solar cells, including nanowires and nanotextured substrates for the understanding of materials and processing and for the cost reduction with thin

cells. We showed that nanowires function as well-defined CIGS-CdS p-n junction for understanding the chemical fluctuation, defect formation interface and grain boundary behaviors and the effect of ion diffusion. We have also demonstrated effective nanoscale photon management on nanotextured substrate to provide opportunity for thin CIGS solar cells. We also developed the scalable methods for producing such nanotextured substrates.

Future research includes: 1) Applying the materials and processing knowledge to the best baseline of CIGS solar cell fabrication to improve the efficiency at the module level. 2) Implementing the photon management strategy to the glass substrate used for CIGS solar cells. Demonstrate high efficiency thin CIGS solar cells.

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11) H. Peng, C. Xie, D. T. Schoen, K. McIlwrath, X. F. Zhang, Y. Cui "Order Vacancy Compounds and Nanotube Formation in CuInSe₂-CdS Core-Shell Nanowires" *Nano Lett.* 7, 3734-3738 (2007). (Address Task 1, 2, 3 and 5)