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Patterned honeycomb-like ZnO cavities for Cu(In,Ga)Se_2 thin film solar cells with omnidirectionally enhanced light harvesting

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ABSTRACT

A novel idea was presented by using patterned honeycomb-like ZnO cavities to enhance the light harvesting of Cu(In,Ga)Se_2 (CIGS) thin film solar cells in a broadband wavelength range. Large-scale patterned honeycomb-like ZnO cavities were fabricated through the versatile colloidal lithograhpy technique combined with the subsquent hydrothermal growth reaction. The growth mechanism was proposed based on the structural evolution of the patterned ZnO cavities. By introducing the patterned honeycomb-like ZnO cavities into CIGS solar cells, the performances of the device can be remarkabley improved due to the enhanced light harvesting. Photovoltaic device with a standard soda lime glass (SLG)/Mo/CIGS/CdS/i-ZnO/AZO/ZnO cavities/Ag grid structure exhibited a maximum power conversion efficiency of 11.4% under the standard AM 1.5 global illumination with a light intensity of 100 mW/cm^2. An improvement of over 9.0% in the short-circuit photocurrent density and a 10.6% enhancement in the energy conversion efficiency were achieved compared with the standard reference device without ZnO cavities. More importantly, the device with patterned ZnO cavities exhibited omnidirectional behavior within a wide incident angle range. The enhancement of light harvesting is originating from the novel "negative" configuration of patterned ZnO cavities, which can realize high-efficient light trapping by multiple scattering and light coupling.

1. Introduction

In recent years, energy harvesting by photovoltaic technique has been regarded as one of the most effective ways to solve the energy crisis and mineralize the environmental contaminants [1–3]. Various technologies based on different materials were investigated to develop high-efficient photovoltaic devices. Up to now, single-crystalline silicon solar cell still remained a dominant position in the current photovoltaic market [4,5]. However, the high material cost and complicated fabrication process are two major obstacles for its widespread application [6,7]. By contrast, thin film solar cells are more attractive due to their better flexibility, lower cost, and cheaper processing.

Several kinds of thin film solar cells, such as gallium arsenide (GaAs), cadmium telluride (CdTe), organic photovoltaic device (OPV), perovskites, and copper indium gallium selenide (CIGS) were received much attention due to their fast and remarkable development recently [8–10]. Among them, CIGS solar cells have been considered as one of the most promising alternative to single-crystalline silicon solar cells from the point view of analogous conversion efficiency and long-term stability in practical use [11]. Various preparation methods are developed to fabricate the CIGS absorbers, such as solution process, electrodeposition, electrostatic spray deposition, co-evaporation and the selenization of sputtered precursor films [12]. A record conversion efficiency of 22.6% has already been attained in a laboratory scale based on the traditional co-evaporation technique by Zentrum für Sonnenenergie und Wasserstoff-Forschung (ZSW) [13]. Despite the broad application prospects of CIGS thin film solar cells, there still exists an obvious performance gap between single-crystalline silicon solar cells. Due to the narrow compositional stability window of CIGS quaternary compound, one of the main challenging tasks is the fabrication of pure-phased CIGS absorber layer with Cu-poor condition [14]. On the other hand, there is a conflicting interplay between their electrical (carries collection) and optical (light absorption) properties due to its film configuration [15]. The thinner CIGS absorber is beneficial for the transportation of carriers and its final collection by electrodes. However, thinner CIGS absorber brings the incomplete absorption of the

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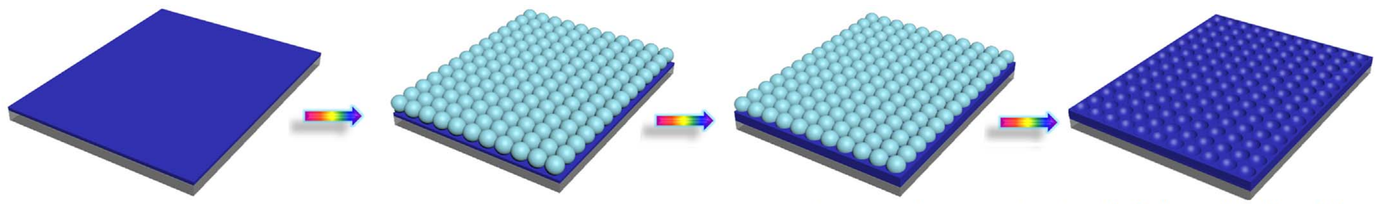

Fig. 1. Schematic illustration for the fabrication of patterned ZnO cavities.

incident light. This dilemma can be solved by further promote the light absorption of CIGS absorbers under optimized film thickness.

Different light trapping techniques have been proposed to manipulate light in thin film solar cells such as the use of photonic crystals, diffraction gratings, plasmonic scatters, Mie resonators, and aperiodic structures [16]. An inverted nanopyramid array was fabricated on the front side of ultrathin crystalline silicon solar cells by S. Collin et al. [17] An optical path enhancement of 10 in the long wavelength range was demonstrated. The low photon escape probability at the front interface (25%) played a key role in the efficient light trapping process. J. Yoon et al. reported the fabrication of hexagonal arrays of titanium dioxide by nanoimprint lithography and dry etching, which deposited on the window layer of GaAs solar cells serving as lossless photonic nanostructures for antireflection, diffraction and light trapping [18]. A transparent polymer microlens array was fabricated on the surface of OPVs by Xue et al., which can increase the light path in the active layer and reduce surface reflection [9]. In contrast, fabrication of traditional light trapping structures in the CIGS absorber layer is difficult due to its necessary selenization procedure under high temperature. The most appropriate scheme is to fabricate nanostructures on the front surface of CIGS thin films solar cells, which can avoid the damage of fabricated nanostructures during the high temperature selenization step. Nanostructures placed on the front side of CIGS thin film solar cell can significantly suppress the reflectance and efficiently enhance the light propagation length of guided mode coupling in wide range of wavelengths. J. Myoung et al. reported the fabrication of bio-mimicked ZnO nanorods and used as antireflection coating for CIGS solar cells [19]. The efficiency was increased from 10% to 11.5%, which was mainly benefited from the gradual increase in the refractive index between air and the inserted ZnO nanostructures. H. Kuo et al. reported the fabrication and characterization of ZnO dandelions on CIGS solar cells [20]. The omnidirectional and broadband antireflections of the proposed dandelion ZnO structure were investigated by using angle-resolved reflectance spectroscope. The short-circuit density was enhanced by 31.87%. Although different nanostructures such as nanotrees, nanowires, and nanotips have been extensively investigated for light absorption enhancement in CIGS thin film solar cells, [21,22] developing a new approach to fabricate nanostructures at low-cost is still highly desired for high-efficient CIGS thin film solar cells.

In this paper, a novel idea of using patterned honeycomb-like ZnO cavities was proposed to enhance the light harvesting of $Cu(In,Ga)Se_2$ (CIGS) thin film solar cells in a broadband wavelength range. Patterned honeycomb-like ZnO cavities were fabricated through the versatile colloidal lithograhpy technique combined with the subsquent hydrothermal growth reaction. The colloidal lithography technique is a well-known, low-cost, and high-throughput fabrication technique for patterned nanostructures. The grow mechanism was investigated based on the structural evolution of the patterned ZnO cavities. The fabricated CIGS device with patterned ZnO cavities exhibited omnidirectional behavior within a wide incident angle range. The typical "negative" configuration of patterned ZnO cavities makes it easier to trap the incident light from all directions due to the photon multiple scattering. Here, the "negative" means that the structures embed into the substrate while the "positive" means the structures protrude out from the substrate into free space. To the best of our knowledge, no research work has been reported to fabricate and discuss the characteristics of CIGS thin film solar cells with patterned honeycomb-like ZnO cavities array. Our findings provide new ways for developing high-efficient CIGS solar cells.

2. Experimental

2.1. Fabrication of patterned ZnO cavities array

In order to investigate the structural evolution and basic optical properties of patterned ZnO cavities, it was fabricated on the glass slide substrate prior to its final application on CIGS thin film solar cells. The glass slide substrates were ultrasonically cleaned by using acetone and methanol, respectively. After drying by blowing N_2 gas, the AZO films were deposited by radio frequency (RF) magnetron sputtering system using a ZnO target mixed with 2 wt% Al_2O_3. The sputtering power was kept at 200 W. The sputtered AZO films were used as seeds in the subsequent hydrothermal growth. Polystyrene spheres (PSs) with diameters of 300 nm were adopted to self-assemble and form a monolayer mask on the seeded glass substrate through the transfer-floating technique [23]. The seeded substrate with PSs monolayer was heated at 90 °C for 30 min to promote the adhesion of the spheres to the substrate. During the hydrothermal growth, the substrate with PSs mask was mounted vertically in a sealed teflon cylindrical container, containing a 35-mL solution of 0.4 M methenamine ($C_6H_{12}N_4$, HMT), 0.4 M zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) and 0.45 mg of sodium citrate. The hydrothermal growth temperature was kept at 60 °C. After the hydrothermal growth, the PSs masks were removed in toluene under gentally ultrasonic treatment. Finally, the patterned ZnO cavities were obtained on the substrate. The schematic illustration for the fabrication of patterned ZnO cavities is presented in Fig. 1.

2.2. Fabrication of CIGS thin film devices with patterned honeycomb-like ZnO cavities

The device fabrication process was similar to our previous reported work except a little modification [24]. In general, the CIGS/CuIn mixed precursor film was firstly sputtered on the Mo coated SLG substrate through a magnetron sputtering system. Two independent radio frequency power supplier (90 W) and direct current power supplier (30 W) were employed to sputter CIGS target and CuIn target, respectively. After selenized by a rapid thermal process using a halogen lamp furnace, a relatively compact and smooth CIGS absorber was fabricated on the Mo substrate with a thickness of about 2 μm. Subsequently, a 50 nm thick CdS buffer layer was deposited on the CIGS absorber by chemical bath deposition and an 50 nm thick intrinsic-ZnO (i-ZnO) was sputtered in sequence. After that, patterned ZnO cavities array was fabricated on the surface of i-ZnO as described in the above section. In order to avoid the damage of pre-sputtered i-ZnO layer, the sputtering power for AZO seed layer was lowered to 125 W. The AZO film thickness was kept at about 500 nm. Finally, the Ag grid electrodes were thermally evaporated through a metal shadow mask as the current collector.