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Design of nano/micro–structured surfaces for efficiently harvesting and managing full–spectrum solar energy

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ABSTRACT

The proposed photovoltaic (PV)–Thermoelectric (TE) hybrid system is an advanced approach to utilize full–-spectrum (300–2500 nm) solar energy. In this system, incident photons in different wavelengths must be transferred to different devices via efficient allocation, which is called photon management, to enhance the performance of the hybrid systems. The photon–management property can be realized through subwavelength structures in solar cells. In this work, based on silicon solar cells, composite subwavelength structures are fabricated in crystalline silicon through ICP etching and magnetron sputtering process with the required spectral characteristics. Integrated ordered, and disordered nanopillar/nanohole arrays enable broadband absorption in the wavelength range (300–1100 nm) above the bandgap with an average absorptance of about 97%. About 60% solar energy from 1200 nm to 2500 nm can transmit to the TE devices with the assistance of the deposited TiO_2/SiO_2 bilayer films on the bottom side. The good photon–management performance is independent of the incident angles and insensitive to the polarization states. The method can also be applied to other kinds of solar cells for the application in the PV–TE hybrid systems. This paper opens new routes to smart photon management, which is expected to have promising applications in efficient full–spectrum solar energy conversion.

1. Introduction

For the strong demands for clean, sustainable and renewable energy, solar energy has gained extensive attention and been studied for several different applications. Photovoltaic (PV) devices are one of the most widely used applications of solar energy. In order to improve the efficiency and reduce the manufacturing cost of various solar cells, photon management is put forward by harvesting light in solar cells to generate more electron–hole pairs (Shang and Li, 2017). Over recent year, various photon–management subwavelength structures have been proposed to obtain efficient light trapping in all sorts of solar cells, such as multilayer anti–reflection films (Aiken, 2000; Li et al., 2014), nanopillars (Hsu et al., 2008; Pudasaini et al., 2013; Wang et al., 2010), nanoholes (Han and Chen, 2010; Lin et al., 2013; Peng et al., 2010), biomimetic structures (Deniz et al., 2011; Leem et al., 2011; Stavenga et al., 2006), nanopyramids (Cheng et al., 2012; Papet et al., 2006), plasmonic structures (Atwater and Polman, 2010; Notarianni et al., 2014; Temple and Bagnall, 2013; Wensheng et al., 2017), and so on. The structures can not only be applied to the surface of the semiconductor materials but also be fabricated with other materials, such as transparent conductive films (Leem et al., 2011; Nowak et al., 2014). Unlike the absorption enhancement caused by the structures fabricated with semiconductor and dielectric materials, the plasmonic structures are mainly placed in or at the bottom of the active layer to obtain absorption enhancement in the infrared wavelength range (Wensheng et al., 2017; Yue et al., 2016). The absorption in the solar cells is significantly enhanced with these subwavelength structures to generate more electron–hole pairs in the active layer by effects like apparent gradient refractive index (RI) (Muskens et al., 2008) to suppress reflection, scattering effect to increase optical path (Garnett and Yang, 2010; Temple and Bagnall, 2013) and plasmonic effects (Atwater and Polman, 2010). Different kinds of structures can be combined together to get a broadband absorption.

However, for utilization of full–spectrum (300–2500 nm) solar energy, there are two main shortcomings in using single PV devices: (i) Due to the bandgap of semiconductor materials, PV devices can only take use of part of the full–spectrum solar energy. (ii) The light absorbed by solar cells will partly be converted to heat as the recombination of electron–hole pairs can result in unavoidable thermalization loss in solar cells (Park et al., 2013). These two aspects limit the performance of PV devices to utilize solar energy in the whole spectrum range. Thus, PV–thermoelectric (TE) hybrid systems were put forward to utilize the unserviceable solar energy and the waste heat in PV devices (Beeri et al., 2015; Wang et al., 2011; Zhu et al., 2016). In this

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system, the solar energy above the bandgap should be efficiently absorbed by solar cells. Meanwhile, the rest solar energy should transmit to bottom TE devices and be absorbed by the hot side of TE devices. This part of solar energy can be converted to heat and will be a heat source of the TE devices. In this way, the below–bandgap solar energy and the thermalization loss in PV devices will be utilized adequately by combining PV and TE devices into a hybrid system. To realize the maximum utilization of solar energy in the hybrid system, the key issue is to allocate the full–spectrum solar energy in different wavelength ranges to different devices, which means that it is pivotal to realize full–spectrum photon management in PV–TE hybrid systems. Nevertheless, the previous works on photon management only considered the absorption enhancement for PV devices. It is a huge challenge to obtain high absorption in the PV devices and high transmission in the rest wavelengths meanwhile. Moreover, the incident angles and polarization states must be taken into account (Dincer et al., 2014; Liu et al., 2013; Mulla and Sabah, 2015). Thus, it is essential to propose dual–-band light management structures to fill the solar full–spectrum bills for PV–TE hybrid applications to ensure remarkable solar energy utilization.

Here, the crystalline silicon (c-Si) solar cell is taken as an example. Based on the solar full–spectrum light harvesting in the PV–TE hybrid systems, a new dual–band photon management is proposed with the assistance of composite subwavelength structures fabricated on a c-Si substrate, which aims to assign photons in different wavelength ranges to different devices in the hybrid system for the solar full–spectrum utilization purpose. On the top side, integrated ordered and disordered nanopillar/nanohole structures are fabricated. This surface structure can realize efficient light–harvesting property for c-Si solar cells in the 300–1100 nm wavelength range due to the scattering between the nanopillars and nanoholes, which enhances light path in the silicon wafer. To further improve the transmittance in the near-infrared (NIR) wavelength range, bilayer films of TiO_2 and SiO_2 are deposited on the bottom side of the wafer, which can enhance the NIR transmittance via gradient refractive index theory to suppress reflection at the material interface. ~97% average absorptance in the wavelength range above the bandgap and ~60% average transmittance from 1200 nm to 2500 nm are obtained in the meantime. The performance shows angle–independent and polarization–insensitive properties for the case of the natural incident sunlight. These novel light management structures distribute the full–spectrum solar energy reasonably for the PV–TE hybrid systems, which realizes the utmost utilization of solar energy. In the long term, this proposed light management can be applied to other kinds of PV cells, and provide an efficient approach for other full–-spectrum light–harvesting utilization.

2. Experimental and simulation methods

2.1. Experimental method

In this work, a unique composite structure is proposed based on single nanopillar and nanohole architectures. The schematic of the fabrication process is given in Fig. 1. Nowadays, there have been various methods to fabricate subwavelength structures on the c-Si (p–type, bandgap: 1.12 eV (~1100 nm), resistivity: 0.05–0.1 Ω cm, doping level: 10e16 cm^{-3}) to harvest light. Most of them are with the help of photomasks and dry etching (Abe et al., 2016; Cecchetto et al., 2013; Chang et al., 2005) or wet etching (Huang et al., 2008; Kim and Khang, 2014; Lachiheb et al., 2014; Papet et al., 2006; Wang et al., 2010) process. Concerning large–area manufacture, the PS sphere self-assembly method (Gao et al., 2015) is used to form the periodic photomask, as PS spheres are insoluble in water and can float on the water surface. The area of PS photomask relies on the area of the water surface. A p-type 400-μm-thick c-Si wafer is first dealt with a hydrophilic treatment, which soaks in a mixed solution consisted of 98 wt% H_2SO_4 and 30 wt% H_2O_2 with the volume fraction of 3: 1 for 15 min. The PS photomask can be easily got by using an injector to push the PS spheres to the water surface slowing. The PS spheres used is 3 w/v% and is 10 times diluted by 50 wt% ethanol solution. During this process, the PS spheres can assemble with Marangoni effect, and the injection speed used is 0.15 mm per minute. Periodic close–packed PS (Diameter ~600 nm) monolayer is obtained via dropping 1 ml Sodium Dodecyl Sulfate (SDS, 5 wt%) solution to the water surface. Finally, after five minutes standing, the PS monolayer is transferred to the surface of the silicon wafer. In this way, a larger–area PS monolayer is obtained through a very low–cost and simple self–assembly method. With the PS monolayer photomask, the dry etching process can be taken to fabricate the subwavelength structures.

Etching process is the commonly used method for subwavelength structure fabrication with different kinds of gas, including fluorine–containing gas and halogen gas, which can react with silicon. Dry etching is more controllable than the wet etching. On this basis, the inductively coupled plasma (ICP) etching process is chosen. For security consideration, the SiF_6 gas is chosen as the reaction gas. During the ICP etching process, it must avoid the photomask from being destroyed. However, the SiF_6 gas shows an isotropous etching characteristic. Thus, to gain vertical nanopillars with high depth–to–width ratio, efforts should be taken to protect the sidewalls of nanopillars from being destroyed during the etching process. For this consideration, BOSCH etching method (Chang et al., 2005) is introduced by adding the C_4F_8 gas in the etching process with the same etching parameters. In the beginning, The SiF_6 gas is used to etch the silicon for 9 s without affecting the verticality of the structures. Then the C_4F_8 gas is taken to passivate silicon to protect the sidewalls of the structures from horizontal etching. Each time for the C_4F_8 etching process is 7 s. The power and flow rate of the SiF_6 gas is 100 sccm and 600/15 W, respectively. By repeating the above two etching steps for 20 times, vertical nanopillars are obtained with high depth–to–width ratio. The diameters of PS sphere are adjusted by the plasma etching (PE) process with the oxygen (Plettl et al., 2009). The power is 200 W, and the flow rate of the oxygen is 100 sccm. For the fabrication of nanoholes, the photomask is transformed from PS monolayer to the silver film by sputtering a silver film to the present surface. The magnetron sputtering is employed at 0.7 Pa, and the sputtering power is 60 W. Finally, the periodic hollow nanopillars can be gained after a lift–off process of PS spheres and ICP etching with the same etching parameters.

The fabrication of the bottom TiO_2/SiO_2 bilayer films is also through the magnetron sputtering. For the TiO_2 film, the titanium target is used with the direct current sputtering at 0.8 Pa pressure. The power is 400 W, and the flow rate of $Ar:O_2$ is 8:1. For the SiO_2 film, the glass target is used with the radio–frequency sputtering at the same pressure and flow rate ratio. The sputtering power is 200 W.

The full–spectrum optical properties (absorption and reflection spectra) are measured with an integrating sphere (Agilent Cary 5000 UV–VIS–NIR spectrophotometer). The transmittance can be got directly as 1 – absorptance – reflectance. For the AM1.5G solar irradiance, the absorptance in the wavelength of 300–1100 nm and the transmittance in the wavelength range of 1100–2500 nm are finally obtained.

2.2. Simulation method

The finite difference time domain (FDTD) method is used to solve Maxwell equations in the simulated region. In the simulation, the simulated region is one unit of the ordered nanopillar arrays under the AM1.5G light source. In the x and y directions, periodic boundary conditions are used, and a plane wave is set from 300 nm to 1100 nm in the z direction, which is regarded as the light source. A monitor is placed above the light source to get the reflectance from the surface. The top and bottom boundary conditions are both perfect matched layers (PML).