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Broadband photon management of subwavelength structures surface for full-spectrum utilization of solar energy

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ABSTRACT

In this work, advanced photon-management composite subwavelength structures are fabricated to manage solar energy in the full-spectrum (300–2500 nm) wavelength range for the application of the photovoltaic-thermoelectric hybrid systems to fully utilize the solar energy. This proposed photon-management method will simultaneously realize efficient light trapping for the photons with above-bandgap energy in solar cells and the utilization of the below-bandgap photons and the waste heat resulting from the thermalization effect in solar cells with bottom thermoelectric devices. The typical structure is designed: Top ordered hexagonal nanohole arrays can trap above-bandgap photons to enhance the absorption in the silicon wafer, and TiO_2/SiO_2 bilayer films are deposited on the bottom side of the wafer to improve the transmission of the below-bandgap photons. ~97% total absorptance for wavelengths of 300–1100 nm is achieved with optimized diameters of central nanoholes. The total transmittance, on the other hand, is improved to ~60% from 1200 nm to 2500 nm. The results indicate that the structures realize the appropriate allocation of photons within different wavelength ranges to different devices for sufficient utilization of full-spectrum solar energy. This novel full-spectrum photon management benefits from the strong scattering effect among the nanoholes and the gradient refractive index of bilayer films. Moreover, the photon-management performance shows angle-independent and polarization-insensitive characteristics. This method can be applied to various kinds of solar cells for photovoltaic-thermoelectric hybrid systems and may provide thoughts for other solar harvesting applications.

1. Introduction

Solar energy, which is a kind of renewable and abundant energy, has gained wide attention due to the intense needs for clean energy. Various utilization methods of solar energy have been proposed. At present, the photovoltaic (PV) device is one of the most popular approaches for solar energy application. However, the utilization efficiency of full-spectrum (300–2500 nm) solar energy reaching the ground is limited by the bandgap of solar cells. The PV devices can only take use of incident solar energy above bandgap. Furthermore, part of the absorbed light in solar cells will be converted to heat due to the recombination of electron-hole pairs in the active layer or at the surface, which is called thermalization loss [1]. This recombination process will cause the increase of the temperature of solar cells, and further brings down the usage of solar energy. To break these limitations in PV devices, a novel PV-thermoelectric (ThE) hybrid system has been proposed to improve the utilization efficiency of full-spectrum solar energy, which combines PV devices and ThE devices into a hybrid PV-ThE system. A concentrated PV-ThE hybrid system was systematically analyzed by Lamba and Kaushik [2] with the influences of thermocouple numbers, the irradiance, PV and ThE current. Hsush et al. [3] proposed a $CuInGaSe_2$ (CIGS)/ThE device with the efficient of 22% by employing passive light-trapping ZnO nanowires. Zhang and Yin [4,5] systematically investigated the influences of the thermal resistances on the hybrid system under the circumstance of high concentration ratio. In this system, the first-line goal is to allocate the full-spectrum solar energy to different devices. The solar energy above the bandgap must be absorbed by PV devices efficiently, and the other part should transmit to ThE devices. Photon management is a reasonable approach to realize the performance in hybrid systems. Recently, all sorts of photon-management subwavelength structures have been widely investigated to trap light in PV devices, including anti-reflection films, biomimetic structures, nanopillars, nanoholes, nanocones, nanopyramids, and plasmonic structures. The sizes of these structures are comparable to the wavelengths of solar spectrum and can lead to various excellent light-trapping effects due to light-matter interactions. Anti-reflection coatings were proposed the earliest to suppress the reflection by smoothing the change of refractive index from the air to

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materials. Makableh et al. [6] fabricated an optimized ZnO film on the GaAs solar cell through the sol–gel method. The enhancement could be seen in spectral properties, conversion efficiency and the external quantum efficiency (EQE). Similar indium oxide films front contact was used to enhance the opto-electrical properties of heterojunction solar cells [7]. Kanda et al. [8] introduced an Al_2O_3/TiO_2 double layer coating, and the reflection in the visible wavelength range was suppressed efficiently. Elshorbagy et al. [9] designed a customized Si_3N_4 coating with a 15.2% enhancement of the short circuit current. Various structured solar cells have developed rapidly with the discovery of moth-eye structures in solar cells, which could be attributed to the effective gradient refractive index, including nanocones and nanopyramids. The influences of the sizes of the moth-eye structure on the optical properties of thin-film silicon have been studied [10,11]. The moth-eye pattern could also be prepared on the surface of the Polydimethyl siloxane (PDMS) or polymethyl methacrylate (PMMA) film through the nanoimprint technology for the application of organic solar cells [12]. The same technology is employed to fabricate nanocone structures for high-efficiency CdS/CdTe solar cells [13]. Li et al. [14] applied the nanopyramid structure to a tandem silicon solar cell, which led to a remarkable improvement of the short circuit current density in both the top and bottom cells. Moreover, Zada et al. [15] fabricated nanostructures on the surface of a TiO_2 film inspired by cicada wings with angle-independent anti-reflection properties. Nanopillars, nanoholes and gratings are typical structures for trapping light in solar cells as well. The light-trapping effect in these varieties of structures is attributed to the strong scattering between structures to increase light path in solar cells and generate effective optical coupling. He et al. [16] found that both the absorption and open circuit voltage were enhanced for organic-silicon heterojunction solar cell. Chen et al. [17] studied the light-trapping effects of nanohole arrays with different depths on the performance of silicon PV devices and found that the depth of 700 nm was sufficient for the optimal light-trapping effect. Besides these structures based on dielectric and semiconductor materials, metallic structures, such as metallic nanoparticles, gratings and metamaterials, have been revealed to provide advanced light trapping with specific plasmon effect. Clavero [18] gave the fundamentals of the hot-electron generation and regeneration process in plasmonic structures, which was the key point to get high-efficiency photovoltaics. Hsu et al. [19] studied the performance of different shapes of silver nanoplates embedded in organic and perovskite solar cells. With the aid of the surface plasmon resonance of the nanoplates, the power conversion efficiency was enhanced in both kinds of solar cells. Massiot et al. [20] used fishnet plasmonic absorber to excite surface plasmons for the perfect absorption in the GaAs solar cell. The application of these subwavelength structures is a quite efficient trick to enhance the PV efficiency and reduce the cost. Although these plasmonic structures can improve the absorption in materials, they will cause an unavoidable heating problem, which is an undesired loss for PV devices. This kind of loss was discussed by Vora et al. [21] to obtain the maximum useful absorption. Nevertheless, most researches only focus on the wavelength range above the bandgap for PV applications, and there are few reports to study the utilization of below-bandgap photons in the hybrid systems. It is a big challenge to get high transmission in the wavelength below the bandgap simultaneously with omnidirectional and polarization-insensitive properties [22,23]. Therefore, subwavelength structures should be developed to provide proper full-spectrum photon management for PV-ThE applications. High absorption for the above-bandgap wavelengths is to ensure the high efficiency of solar cells. The efficient transmission should be obtained to be the heat source of the ThE module, as well as the heat in the solar cells. The improved conversion efficiency of solar energy can be achieved for this hybrid system with the assistance of the proposed photon management.

Based on this prior and crucial research work, in our present study, we propose a new method of photon management for full-spectrum light harvesting in PV-ThE hybrid applications. This photon management can be realized through fabricated subwavelength structures with high absorption in the above-bandgap wavelength range and high transmission in the rest wavelengths, which also presents angle-independent and polarization-insensitive characteristics. In this way, both the full-spectrum solar energy and heat in solar cells will attribute to the power conversion efficiency of the hybrid system. The photon-management subwavelength structures consist of top novel hexagonal nanohole arrays and bottom bilayer films on a 400–μm-thick crystalline silicon (c-Si) wafer. On the top surface, novel hexagonal nanohole arrays are fabricated through the large-area polystyrene (PS) self-assembly method and Bosch deep silicon etching process. On the bottom side of the wafer, TiO_2/SiO_2 bilayer films are used to increase the transmittance for wavelengths of 1100–2500 nm. With fabricated composite subwavelength structures, near 97% total absorptance in the wavelength range of 300–1100 nm and about 60% total transmittance from 1200 nm to 2500 nm are obtained simultaneously. The light-trapping property in the above-bandgap wavelength range is analyzed through the finite difference time domain (FDTD) simulations. The impacts of incident angles and polarization states on the spectral characteristics are also investigated.

2. Experimental and simulation methods

2.1. Experimental process

At first, a c-Si wafer (p-type, bandgap: 1.12 eV (~1100 nm), resistivity: 0.05–0.1 Ω cm, doping level: 10e16 cm^{-3}) is dealt with the hydrophilic treatment for the preparation of the etching mask, which is soaked in a mixed solution consisted of concentrated sulfuric acid (H_2SO_4) and the hydrogen peroxide (H_2O_2) (the volume fraction of H_2SO_4 (98 wt%): H_2O_2 (30 wt%) is 3:1) at 90 °C for 15 min, and then ultrasonically cleaned by the acetone, ethanol and deionized (DI) water, successively. The area of the c-Si wafer is 30 mm × 30 mm. Over recent years, various types of technologies have been proposed for the manufacture of micro/nanostructures, such as metal-assisted catalyst etching (MACE), nanoimprinting, photolithography, electron beam lithography. Han et al. [24] gave a review of recent advances in MACE of silicon and the applications of these fabricated structures for sensors, energy storage and conversion. Nanoimprint technology is a prospective method for the fabrication of large-area and periodic structures [25] with enhanced light absorption to improve the power conversion efficiency. Sivasubramaniam and Alkaisi [26] obtained inverted nanopyramid structures through the combination of the interference lithography and relevant pattern transfer technologies. The electron beam lithography is a quite flexible method to get various complex and composite structures [27], whereas the cost of this technology is too expensive to be employed to the commercial production. Al-Douri et al. [28] also created CdS random nanostructures through simple sol–gel spin coating technique with remarkable optical properties. In our work, the Bosch deep silicon etching process [29] is employed to fabricate the novel top hexagonal nanohole arrays with periodic polystyrene (PS) masks made through the large-area PS sphere self-assembly method [30]. The schematic of the fabrication process is provided in Fig. 1. The PS spheres have unique characteristics as they can float on the water surface. On this basis, the PS monolayer can be obtained through the self-assembly process on the water surface. The original PS spheres are stored in ethanol, and the concentration and diameter are 2.5 w/v% and 600 nm, respectively, and this ethanol suspension is driven to the water surface with an injector. The spheres then can spread out slowly on the water surface according to the Marangoni effect. In order to obtain a high-quality PS monolayer, the PS dispersed suspension is 10 times diluted by 50 wt% ethanol solution and the diluted suspension is ultrasonic dispersed to avoid the agglomeration of PS spheres. The injection rate is 0.15 mm per minute, which is controlled by a pump. At the end of the injection process, 20 drops of Sodium Dodecyl Sulfonate (SDS) solution is dropped to the water surface to accomplish the self-