

# Preparation of structured surfaces for full-spectrum photon management in photovoltaic-thermoelectric systems



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## ABSTRACT

Micro-structured surfaces for broadband and omnidirectional photon management in photovoltaic-thermoelectric systems are fabricated on the silicon wafer by inductively coupled plasma etching with self-assembly polystyrene spheres mask, KOH solution etching and magnetron sputtering method. The Si antireflection structure coated with SiO<sub>2</sub> film is fabricated on the top surface of Si substrate to enhance the absorption of the photons with wavelengths of 0.3–1.1 μm is increase the electron-hole pairs. The TiO<sub>2</sub>/SiO<sub>2</sub> films as the back-antireflection coating are deposited at the back of Si wafer to improve the transmission of solar energy within the wavelength range of 1.1–2.5 μm. The absorbed photons within the wavelength range of 0.3–1.1 μm can directly be converted into electricity power by Si solar cells while the photons with wavelengths of 1.1–2.5 μm transmit through the cells and are utilized by thermoelectric modules. The effects of etching parameters on the spectral features are investigated to get the optimal etching parameters. With the optimal etching parameters, the surface absorption for the wavelengths of 0.3–1.1 μm is significantly increased to above 0.95 due to the effective graded refractive index and the transmission is obviously enhanced for the wavelengths of 1.1–2.5 μm. The incident angle-sensitivity and polarization-sensitivity of the fabricated structured surfaces are analyzed. The results indicate that these surfaces can be selected for photovoltaic-thermoelectric systems due to their high omnidirectional absorption and transmission of the photons as well as the favorable polarization-insensitivity within the expected wavelength ranges.

## 1. Introduction

Suppression of surface reflection is important for photovoltaic (PV) solar cells because of the great reflective energy loss resulted from the refractive index difference at the interface between PV cell and air [1]. Single- and multi-interference coatings are traditionally used to reduce the surface reflection. However, the interference coatings can only reduce the reflection at specific wavelength or within a narrow wavelength band over a limited incident angle range [2]. Consequently, great efforts have been invoked into the investigation of anti-reflection structured surfaces in the field of solar cells for purpose of broadband antireflection, such as gratings, nanowire, nanocone, nanorods, nanoporous and hole array [3–10]. The subject of these micro-structured surfaces is to construct the graded refractive index at the substrate/air interface. Then, the broadband antireflection can be realized. Si cell is a most important solar cell because of the abundant amount of Si material on the earth as well as mature manufacture process of Si cell [11]. Several approaches have been developed to fabricate structured surface for silicon cells, such as photolithography [12], electron-beam litho-

graphy [13], laser lithography [14] and nanoimprint lithography [15,16]. As a common downside, these techniques are difficult to be widely and actually used because of expensive facilities and complex process [17]. Thus the simpler and more inexpensive procedure is desirable in fabrication of structured surface of Si solar cells. Self-assembly technique based fabrication method is a promising way in preparing the structured surface of Si cell. The self-assembled masks, which were consisted of colloidal nanospheres, metal nano-particles, and porous membrane, were applied to the reactive ion etching (RIE) and the antireflection structured surfaces were successfully fabricated [18–22]. The broadband surface antireflection was finally achieved. Colloidal polystyrene (PS) sphere has great advantage in self-assembled mask for its simply synthesis, low price as well as stable performance. Hence it was widely utilized in the self-assembly technique based fabrication of micro-structured surface. For example, Jiang et al. fabricated moth-eye structured surface on the crystal silicon substrate with self-assembly PS sphere mask and RIE method. The reflection for the wavelengths of 0.4–1.1 μm was reduced to below 0.025 [23]. Yang et al. prepared periodic nanocone, nanorods on the silicon substrate.

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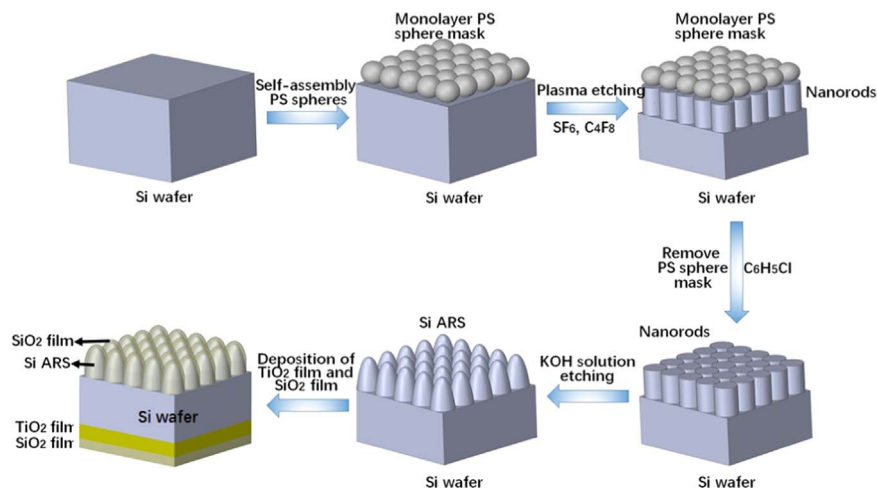


Fig. 1. Schematic diagram of self-assembly based fabrication procedure of antireflection structured surface for Si solar cell in PV-TE systems.

The surface reflection was significantly reduced to below 0.01 [24]. However, the investigation of Si solar cells is mainly focused on the light trapping for the wavelengths of 0.3–1.1  $\mu\text{m}$  while the energy from the solar radiation is confined for the wavelengths of 0.3–2.5  $\mu\text{m}$ . The solar energy with wavelength of 1.1–2.5  $\mu\text{m}$ , which occupies 20% of the full-spectrum solar energy, cannot be utilized by the cells.

Photovoltaic-thermoelectric (PV-TE) system is a promising way to achieve full-spectrum solar energy utilization. When the sunlight strikes the PV-TE system, the PV cell absorbs the photons within the working wavelength band and realizes photon-electric conversion. The TE module absorbs the photons in the infrared band as well as the heat in the system and accomplishes the thermoelectric conversion [25–27]. Plenty of investigations have been devoted to the PV-TE systems to maximum the efficiency of solar energy utilization. According to the investigation of Sark, the conversion efficiency was increased by 8–23% by combining TE module with the PV cell [28]. A theoretical model was proposed by Liao et al. to estimate the performance of the PV-TE system [29]. It was found that the PV-TE system provided higher conversion efficiency along with more electricity output than a separate PV cell or TE module. In the previous research, the PV cell is closely stacked on the TE module [28–32]. The photon management is quite important for the PV-TE system to maximize the energy utilization. The optimal photon management has been hardly investigated. Recently, Zhang and Xuan [33] proposed a photon management scheme for the photovoltaic-thermoelectric system for full-spectrum solar energy utilization. According to their research, the photons within the working wavelength band were absorbed by PV cell while the photons in the infrared band transmitted the PV cell and were used by TE module. However, there is little experimental investigation on the photon management in PV-TE system until now. Hence, it is significant to investigate the fabrication of the structured surface for the photon management of PV-TE systems to maximum the efficiency of solar energy utilization.

Due to the changing incident angle of solar light, it is attractive to design and fabricate the structured surface of the solar cell for the omnidirectional light trapping to enhance the performance of the solar cell in a wide incident angle range. Because the natural solar light includes all polarization states and the polarization can influence the spectral features of structured surface remarkably at oblique incidence, the structured surface is desired to possess the polarization-insensitivity as well as omnidirectional spectral behavior.

Yet up to now, the photon management in PV-TE systems to achieve full-spectrum solar energy utilization is mainly focused on the theoretical research. The experimental investigation is little carried out. The omnidirectional and polarization-insensitive characteristics of broadband photon management in PV-TE systems are hardly experimentally studied.

In this work, we describe the fabrication of structured surface for the silicon solar cells to realize the broadband and omnidirectional photon management in PV-TE systems. The colloidal mask is prepared by self-assembly technique with PS nanospheres. Then the nanorods structure at the top Si/air surface is created by inductively coupled plasma (ICP) etching method, which is the improved procedure of RIE etching. In order to form the better effective graded refractive index, the nanorods structure is modified by KOH solution to create Si antireflection surface (ARS). Then a thin  $\text{SiO}_2$  film is deposited along the profile of Si ARS by magnetron sputtering method to enhance the light trapping performance furthermore. The  $\text{TiO}_2/\text{SiO}_2$  films, which are deposited at the bottom Si/air surface by magnetron sputtering method, decrease the bottom surface reflection and subsequently the transmission in the infrared band is enhanced. The effects of etching parameters on the surface morphology and spectral features are investigated. The incident angle dependence and polarization-sensitivity are analyzed.

## 2. Preparation details

### 2.1. Materials

The reagents used without any further treatment are all quality reagents. Ethanol, Chlorobenzene, deionized water and hydrogen peroxide (30 wt%) are acquired from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). The sulfuric acid (98 wt%) and KOH powder is bought from Shanghai Lingfeng Chemical Reagent Co., Ltd (Shanghai, China). The sodium dodecyl sulfate (SDS) is purchased from Shanghai Aibi Chemical Reagent Co., Ltd (Shanghai, China). The PS sphere solvent (2.5 wt%) is obtained from Tianjin Baseline Chromtech Research Center (Tianjin, China). Si wafers are obtained from Shunsheng Electronic Technology Co., Ltd (Hangzhou, China).

### 2.2. Preparation method of structured surface for photon management

The antireflection structured surface of Si cells is fabricated by following the process schematically shown in Fig. 1. First, the PS sphere monolayer, which is the shadow mask in the following ICP process, is prepared on the Si wafer. Once the PS sphere mask is prepared, the sample is etched by ICP etching process with  $\text{SF}_6$  and  $\text{C}_4\text{F}_8$ . The surface morphology of sample can be adjusted by changing the size of PS sphere and etching conditions. After ICP etching process, the PS sphere mask is removed by  $\text{C}_6\text{H}_5\text{Cl}$  and the close-packed nanorods structure is prepared on the surface of sample. Then the Si nanocone ARS is fabricated on the top Si/air surface by etching the nanorods with KOH solution. At last, the thin  $\text{SiO}_2$  film is deposited on the top Si surface by magnetron

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