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Fabrication and photoelectrochemical properties of ordered Si nanohole arrays

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ABSTRACT

Large-area highly ordered silicon nanohole (SiNH) arrays on Si substrate have been fabricated by the combination of nanosphere lithography and metal assisted electroless etching. The diameter, length of nanoholes, and the center-to-center distance of adjacent nanoholes, can be accurately controlled by nanosphere lithography and metal assisted electroless etching conditions. The sub-wavelength structure of SiNH arrays had excellent antireflection property with a low reflectance of 3.5% within the wavelength range of 300–1000 nm. Compared to the planar Si, the SiNH samples exhibited a higher photoelectrochemical hydrogen generation performance. The improved performance was attributed to SiNH arrays providing an effective light-trapping and a higher semiconductor/electrolyte interface areas which reduce the overpotential required for photoelectrochemical hydrogen reaction. Furthermore, decorating the SiNH arrays with platinum nanoparticles (PtNPs) yielded a significantly high photovoltage of 0.12 V. The photoconversion efficiency of Pt-decorated SiNH (Pt/SiNH) arrays was 22% under the illumination of 100 mW/cm^2, higher than that of SiNH arrays (15.5%) and the planar Si (8.1%).

1. Introduction

Climate change and energy crisis have attracted extensive public attentions in recent years, and therefore, the development of sustainable and renewable energy, especially solar energy, is a key concern. Photoelectrochemical (PEC) water splitting by sunlight for hydrogen production is considered as one of the most promising approaches for using solar energy [1–6]. Among various materials, silicon is an earth-abundant, relatively low-cost semiconductor material suitable for the photocathode of a PEC system that produces hydrogen [7–9]. However, more than 30% of incident light is reflected away from the silicon surface due to its high reflective index, which will greatly reduce the production of photo-generated electron–hole pairs [10]. To maximize the conversion of solar energy into hydrogen, a low reflectance Si surface with periodic nanostructures should be applied. Great efforts have been made to fabricate Si nanostructure and ordered Si nanostructure arrays [11–18]. Many kinds of silicon nanostructures such as nanoparticles, nanopillars, nanotips, nanoholes and nanowires, which offer substantial potential for new device structures, have been applied in the fields of electronics, optoelectronics, photovoltaics and energy storage in the past decade [19–25]. Among the proposed structures, SiNH arrays have theoretically shown better light absorbability because of the strong optical diffraction and coupling [26]. Moreover, compared with the free-standing Si nanostructures which are fragile and easily cracked, SiNH geometry created on Si substrates exhibits superior mechanical robustness.

Numerous methods have been developed to fabricate SiNH arrays, such as electrochemical etching [27], reactive ion etching (RIE) [28], and silicon double inversion [29]. However, RIE method is less suited for making pores with a large aspect ratio, while silicon double inversion method is quite complex and costly since it requires noncomplementary metal oxide semiconductor equipment. The ability to achieve fine control of characteristic parameters using a simple and low-cost method remains a key challenge in the fabrication of SiNH arrays. At present, Si nanowires can be readily achieved through metal assisted electroless etching, a simple and inexpensive method which is able to produce high aspect ratio Si nanowires [30,31]. And this method can be extended to fabricate periodic SiNH arrays on silicon substrate by pre-patterned metal catalysts on substrate surface. In short, Si substrate using the patterned metal gold or silver dots as catalyst is immersed in the solution consisting of deionized (DI) water, hydrofluoric acid (HF), and hydrogen peroxide (H_2O_2). This method can produce ordered SiNH arrays on any conduction type Si

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substrates. Peng et al. [13] reported the fabrication of highly uniform SiNH arrays based on metal assisted electroless etching and deep ultraviolet lithography (UVL). However, the method using UVL to vary the periodicity and dimension of nanoholes is fairly complex and the throughput is low.

Herein, highly ordered SiNH arrays have been fabricated by combining metal assisted electroless etching with the widely used nanosphere lithography method. The diameter of nanoholes and the center-to-center distance of adjacent nanoholes have been accurately controlled by varying the size of polystyrene (PS) nanospheres. By controlling the etching conditions, the desired nanohole length could also be achieved. In addition, we utilized electroless deposited PtNPs to decorate SiNH arrays surface, and compared the PEC properties of three types of Si-based PEC cells (the planar Si, SiNH arrays and Pt/SiNH arrays). Although some studies have used Pt/porous Si [32] and Pt/Si nanowires [33] as photocathode for PEC hydrogen generation, to the best of our knowledge, here is the first report to investigate hydrogen generation on Pt/SiNH photocathode.

2. Experimental methods

2.1. Fabrication of ordered SiNH arrays

The overall fabrication process of ordered SiNH arrays was schematically depicted in Fig. 1. First, p-type Si (1 0 0) wafers with thickness of 300 μm and resistivity of 1–10 Ω cm were used as substrates. The Si wafers were ultrasonically cleaned in acetone and ethanol for 10 min and 5 min, respectively. A monolayer of PS nanospheres template was deposited on the silicon surface according to the technique described by Zhang et al. [34]. Second, an oxygen plasma etching process (10–30 min at 180 W) was used to reduce the diameter of PS nanospheres. The periodicity and diameter of SiNHs were determined by the original and reduced diameter of PS nanospheres, respectively. Third, a 20 nm-thick chromium (Cr) thin film was deposited on the Si wafer by high vacuum electron beam evaporation. Since the etched PS nanospheres were not in contact with each other, the deposited Cr filled the interstitials to form a continuous film with a hexagonal array of holes. Fourth, after the Cr deposition, the PS nanospheres were removed from the substrate by $CHCl_3$ in an ultrasonic bath for 2 min. A continuous metal film with periodic nanohole arrays was then obtained. Fifth, Au particles were deposited into the nanoholes by using electroless Au deposition in a solution containing 50:1(v/v) HF solution and $NaAuCl_4$ (0.002 M). Finally, the regular arrays of Au metallic disks were used as catalyst for silicon etching in aqueous HF solution containing oxidizing agent, and then ordered SiNH arrays were produced on Si wafer. Briefly, the chemical wet etching was carried out in a solution consisting of 10 wt% HF and 1.5 wt% H_2O_2 for a given time, depending on the required nanoholes length. After the etching process, SiNH arrays were washed in a mixture solution of $Ce(NH_4)_2(NO_3)_6$ and $HClO_4$ to remove the Cr at the top of the holes wall. The remaining Au was removed by immersion in boiling aqua regia (3:1 v/v HCl/HNO_3) for 10 min.

2.2. Characterization of SiNH arrays

The morphologies of the samples were characterized by a FEI Quanta 200F field emission scanning electron microscope (SEM) with an accelerating voltage of 0.5–30 kV. Optical reflectance spectra were recorded by a Varian Cary 5000 UV-vis spectrophotometer.

2.3. Fabrication of SiNH and Pt/SiNH photoelectrodes

For PEC measurement, the photoelectrode was prepared by depositing a 500 nm-thick aluminum layer on the Si wafer backside, and annealing at 450 °C for 1 min in nitrogen atmosphere. The resulting electrode was attached to a silver wire with 0.2 mm diameter using silver paint. The silver wire was insulated in a glass tube (0.5 mm diameter). Except the area that was defined as projected area of photocathode, the remaining area of the Si sample was encapsulated using epoxy resin. In order to decorate the SiNHs with PtNPs catalyst, the SiNH samples were immersed into a solution containing 50:1(v/v) HF solution and H_2PtCl_6 (0.001 M), and then rinsed with DI water, dried with N_2.

2.4. Photoelectrochemical measurements

Photocurrent measurements were performed in a solution containing H_2SO_4 and 0.5 M K_2SO_4 (pH 1) electrolyte using a typical three-electrode electrochemical cell configuration. Planar Si, SiNH and Pt/SiNH photocathodes were respectively used as a working electrode, Pt foil was used as a counter electrode, and a saturated calomel electrode (SCE) was used as a reference electrode. Before photocurrent measurement, all the photocathodes were treated by keeping electrode potential constant at −1.2 V vs. SCE for 5 min

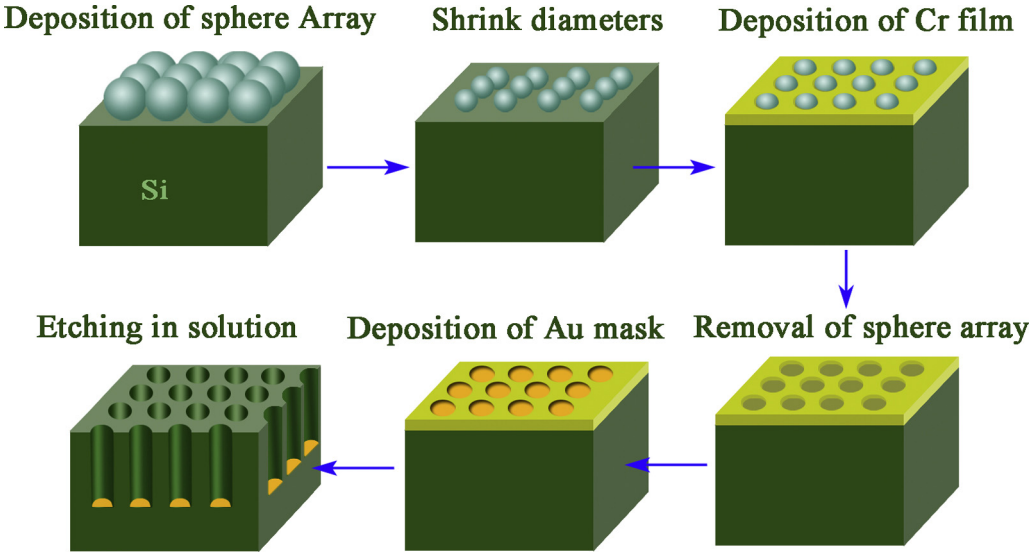

Fig. 1. Schematically illustrating the fabrication process of SiNH arrays.