Materials Letters 125 (2014) 28–31

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Silicon nanowires fabricated by porous gold thin film assisted chemical etching and their photoelectrochemical properties

Lifeng Liu *, Xiao-Qing Bao

International Iberian Nanotechnology Laboratory (INL), Av. Mestre Jose Veiga, 4715-330 Braga, Portugal

ARTICLE INFO

Article history:
Received 16 January 2014
Accepted 23 March 2014
Available online 29 March 2014

Keywords:
Silicon nanostructures
Metal assisted etching
Nanoporous gold
Solar hydrogen evolution
Photoelectrochemistry

ABSTRACT

Nanoporous gold thin films fabricated by dealloying commercially available 12 kt gold leaf have been utilized as masks to catalyze the formation of silicon nanowires from p-type silicon wafers in a HF/H_2O_2 mixture. The resulting silicon nanowires are found to be 40–100 nm in diameter and highly porous with an average pore diameter of ca. 4 nm. These nanowires are used as photocathodes for solar hydrogen evolution, and are found to exhibit a photocurrent as high as 6.05 mA cm^{-2} at a potential of 0 V versus reversible hydrogen electrode (RHE), which is >30 times higher than that of the planar silicon of the same type. The electrochemical impedance spectroscopy result shows that the charge transfer resistance of the nanowire photocathodes is much smaller than that of the planar silicon, revealing a favorable charge transfer kinetics.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Silicon nanowires (SiNWs) have been extensively investigated in the past two decades for their unique electronic, optical, catalytic, electrochemical and photoelectrochemical properties which can find many applications in nanoelectronics [1], biosensors [2], photocatalysis [3], lithium-ion batteries [4], solar cells [5] and photoelectrochemical cells [6–8]. Various methods have so far been used to fabricate SiNWs including chemical vapor deposition [9,10], molecular beam epitaxy [11], electrodeposition [12], supercritical point drying [13] and metal assisted chemical etching (MACE) of silicon [14], among which the MACE has recently attracted tremendous interest because it is a very simple, low cost method allowing for the fabrication of high quality SiNWs with controlled dimensions and orientations [14].

Central to the MACE process is to pattern the Si surface with a porous mesh of noble metals such as Ag, Au or Pt, which usually can be achieved through optical lithography [15], nanosphere lithography [16], polymer lithography [17], laser interference lithography [18] or porous alumina masking [19]. These lithography and masking techniques involve complicated steps toward patterning and are usually time-consuming. Although the MACE can also be achieved in a simpler way using the mixture of hydrofluoric acid (HF) and noble metal salts (e.g. $AgNO_3$) as etchant [14], thus-obtained NWs generally have a rather wide size distribution and also a non-uniform diameter for individual NWs from one end to the other.

In this work, we for the first time use the dealloyed nanoporous gold (NPG) thin film as both a mask and catalyst to fabricate SiNWs via MACE. The obtained NWs are porous, uniform in diameter and highly crystalline. Moreover, they exhibit excellent photoelectrochemical performance towards solar hydrogen evolution, compared with planar silicon of the same type.

2. Materials and methods

The AuAg alloy foils (12 ct, 50 wt% Au) were purchased from Wrights of Lymm Ltd., and have a nominal thickness of 100 nm. The dealloying was performed by floating the alloy foils onto concentrated nitric acid (70%, Sigma) in a petri dish for a certain period of time (typically 2–4 h). Afterwards, the nitric acid was carefully removed using a pipette, and the dealloyed foil was washed with deionized water with caution for three times before it was transferred onto a p-type Si substrate (B-doped, 8–15 Ω cm) which was dipped in a 2% HF solution for 5 min prior to use. The MACE was carried out in a mixture of HF and H_2O_2 (v/v 12:1) at room temperature for 30 min. Afterwards, the wafer was thoroughly rinsed followed by emerging into a gold etching solution ($KI:I_2:H_2O=4$ g:1 g:40 ml) to remove the NPG masks.

The samples were characterized by scanning electron microscopy (SEM, FEI Quanta 650) and transmission electron microscopy (TEM, FEI Titan ChemSTEM80-200, probe corrected). The reflectivity was measured using a UV–vis spectrometer (Shimadzu

* Corresponding author. Tel.: +351 253 140112; fax: +351 253 140119.
E-mail address: lifeng.liu@inl.int (L. Liu).

http://dx.doi.org/10.1016/j.matlet.2014.03.145
0167-577X/© 2014 Elsevier B.V. All rights reserved.

UV-2550) equipped with an integration sphere (Shimadzu MPC2200). The photoelectrochemical properties of the as-fabricated SiNWs were studied in a three-electrode configuration with the SiNW array as a working electrode (i.e. photocathode), a Pt coil as a counter electrode and a saturated calomel electrode (SCE) as a reference. The electrolyte consists of 0.5 M K_2SO_4 solution buffered at pH=1 using sulfuric acid. The current density–potential (J–U) profiles were recorded using a Zennium electrochemical workstation (Zahner) under both dark and light conditions. All the potentials are reported versus reversible hydrogen electrode (RHE) by converting the measured potentials versus SCE through the equation: $U_{RHE}=U_{SCE}+0.241\ V+0.059\cdot pH$ [20]. The electrochemical impedance spectroscopy (EIS) study was done under illumination at 0 V vs. RHE with an AC perturbation of 10 mV. The light source was a calibrated tungsten light working at 100 mW cm^{-2} (Zahner).

3. Results and discussion

Fig. 1a represents a typical SEM micrograph of the NPG thin films, in which a bicontinuous interconnected microstructure can be clearly seen. As reported before, the pore size and ligament dimension of NPG can be readily tuned by using AuAg alloy foils with different compositions for etching [21]. In this way, the size of the resulting SiNWs can also be adjusted. At a given composition, extending the dealloying time, to a certain extent, can change the size of nanopores as well [22], which will also result in Si NWs with different diameters. Fig. 1b is a top view SEM image of the as-fabricated SiNW arrays. It is seen that the NWs are vertically aligned and stick together at their top ends due to surface tension upon drying [17]. A closer look in Fig. 1c reveals that the shape of the cross-section of the NWs replicates that of the nanopores with high fidelity. Unlike the MACE process carried out with isolated metal nanoparticles [14], individually separate SiNWs are exclusively formed upon MACE with a NPG thin film, as revealed in Fig. 1d and e.

The microstructure of the as-fabricated SiNWs was further investigated by TEM. As can be seen from the overview TEM micrograph shown in Fig. 2a, the as-fabricated SiNWs have a broad distribution in their diameters, which is consistent with the broad size distribution of the nanopores in NPG. A close inspection shows that these NWs are in fact porous, with a pore diameter of ca. 4 nm, as displayed in a zoomed view TEM image (Fig. 2b). Fig. 2c is a high-magnification TEM image of a single NW, where the porous nature can be observed more clearly. These nanopores arise from the radial injection of holes generated during MACE into the pre-formed NWs, which can usually be observed when low-resistivity Si is used for MACE [23]. Fig. 2d represents a high-resolution TEM image, in which the continuous lattice and grain boundary-free feature unambiguously demonstrate that these NWs are single crystalline, in good agreement with the previous

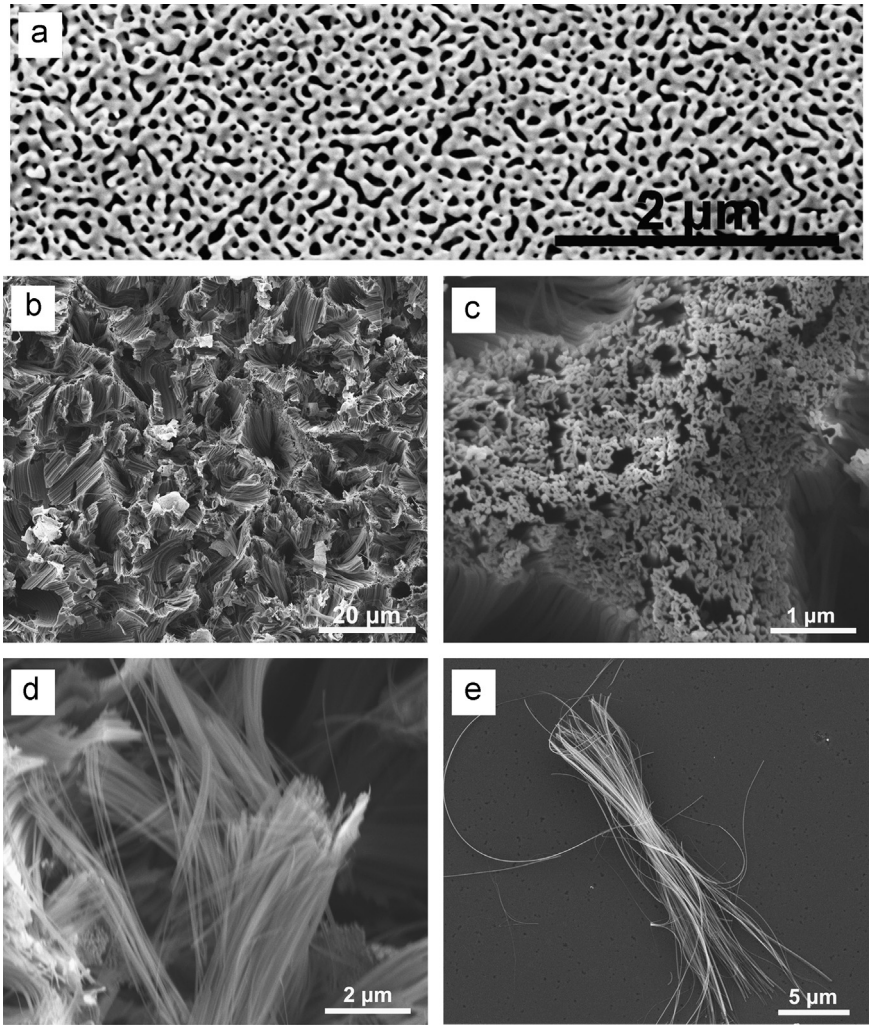

Fig. 1. (a) A typical SEM micrograph of NPG thin films. ((b) and (c)) Top view SEM images of the as-fabricated SiNW arrays. ((d) and (e)) SEM images of SiNW bundles.

Download English Version:

https://daneshyari.com/en/article/1644048

Download Persian Version:

https://daneshyari.com/article/1644048

Daneshyari.com