Available online at www.sciencedirect.com

SciVerse ScienceDirect

Acta Materialia 60 (2012) 2097–2103

Acta MATERIALIA

www.elsevier.com/locate/actamat

Electrochemically controlled fabrication of lightly doped porous Si nanowire arrays with excellent antireflective and self-cleaning properties

Ruey-Chi Wang *, Chien-Yang Chao, Wei-Sung Su

Department of Chemical and Materials Engineering, National University of Kaohsiung, Kaohsiung 81148, Taiwan

Received 11 December 2011; accepted 9 January 2012
Available online 1 March 2012

Abstract

The doping level and morphology of porous Si nanowire (SiNW) arrays are critical for their electrical, optical and surface properties, but preparation of lightly doped porous SiNW arrays with uniform length still remains a challenge. By integrating electroless chemical etching with a proposed electrochemical route, lightly doped single-crystalline porous SiNW arrays with uniform length were prepared from Si wafers with resistivity of 1–770 Ω cm for the first time. Scanning electron microscopy and transmission electron microscopy images show that the size of pores in the NWs is enlarged by increasing the duration of electrochemical process. Based on current–voltage measurements, thermionic emission is proposed to be responsible for the pore formation mechanism. The photoluminescence spectrum of the porous SiNWs shows an obvious peak centered at 680 nm, which is attributed to the quantum confinement effect due to porous structures, evidenced by the shift of Raman peak from 520.7 to 519.7 cm^{-1}. Reflectivity spectra show the average reflectivity of SiNW arrays after electrochemical treatments was further decreased to less than 1.8% in the 350–600 nm wavelength range. Contact angle measurements show that the porous SiNW arrays possess superhydrophobic characteristics with a contact angle of up to 164°. Compared with previous studies, the proposed integrated route can not only prepare uniform, lightly doped, and porous SiNW arrays, but also provide an efficient way to independently control the lengths of NWs and sizes of nanopores in them. The SiNW arrays can be employed as an excellent antireflective and self-cleaning substrate for high efficiency opto-electronic devices.
© 2012 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

Keywords: Porous; Si; Nanowire; Antireflective; Self-cleaning

1. Introduction

Silicon NWs (SiNWs) have attracted tremendous interest over the past decade owing to their one-dimensional morphology and affiliated electrical, photovoltaic and thermal properties. To date, SiNWs have been widely used applied field-effect transistors [1,2], photovoltaics [3,4] and thermoelectrics [5]. Recently, porous SiNWs [6–8], combining the one-dimensional features of NWs and the luminescence properties of porous Si [9], have demonstrated potential for the development of a new generation of silicon-based optoelectronics and photoelectrochemical devices. These porous single-crystalline SiNW arrays were prepared by a metal-assisted chemical etching route. However, a highly doped Si substrate with electrical resistivity less than 0.02 Ω cm is generally required [6–8], which not only raises the cost of materials due to highly doping, but most importantly, also limits the application of NWs. Previous studies have shown that a heavily doped Si layer will cause serious carrier recombination, and thus reduce the efficiency of solar cells [10]. Very recently, a heating metal-assisted chemical etching process was demonstrated in the preparation of lightly doped porous SiNWs with improved opto-electrical properties from Si wafer with resistivity of 1–10 Ω cm [11], but only NWs with a non-uniform length, ranging from 1–10 μm, were formed. The length of NWs and the size of nanopores in them cannot be independently controlled by these one-step chemical etching process so far, no matter whether lightly or heavily

* Corresponding author.
E-mail address: rcwang@nuk.edu.tw (R.-C. Wang).

1359-6454/$36.00 © 2012 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.
doi:10.1016/j.actamat.2012.01.012

doped Si wafers are used. It thus remains a challenge to prepare lightly doped Si porous NW arrays with a uniform length and independently controlled porosity.

In this work, we develop a universal method to fabricate uniform lightly doped porous SiNW arrays for the first time by a proposed electrochemical route. The resistivity of Si wafers employed is further extended to even higher range of 1–770 Ω cm compared with previous studies. By employing an integrated process of metal-assisted chemical etching followed by electrochemical processes, the lengths of NWs as well as the sizes of pores in them can be independently controlled, and the doping concentration of the Si wafers employed can be unrestricted to be highly doped. This preparation scheme can be easily generalized to other porous nanowires. The NW arrays show strong visible luminescence, excellent antireflection and superhydrophobic properties, which can be applied to antireflective self-cleaning opto-electronic devices.

2. Experimental

In this work, n-type Si(1 0 0) wafers with resistivities of 1–5 and 770 Ω cm were employed to fabricate porous SiNWs. First, Si wafers were cleaned by acid solution to remove the organic contaminants on the surface. The oxide layer thus formed was removed in a 48% HF aqueous solution. The cleaned substrates were then immersed in an etching bath containing an aqueous solution of 5 M HF, 0.02 M $AgNO_3$ and 0.2 M H_2O_2 for 1 h to induce the formation of SiNW arrays. To remove residual Ag particles on the surface, the substrates were subsequently immersed in 7.2 M nitric acid for 5 min. Second, electrochemical etching performed in a standard two-electrode electrochemical cell with an aqueous solution of 4 M HF/3.2 M H_2O_2 as electrolyte was carried out to generate nanopores in the NWs. The as-prepared solid SiNW substrate and a bare Si(1 0 0) wafer with the same resistivity were used as anodic and cathode substrates, respectively, for the electrochemical reaction. An external bias of 45 V was applied and the SiNW substrate was etched under a current density of 7×10^{-3} A cm^{-2} for 1–3 min. After electrochemical treatment, the SiNWs were rinsed with distilled water and dried at 50 °C for 30 min.

The SiNWs were examined by field-emission SEM with a Hitachi 4800 for their morphology, and field-emission TEM with a Philips Tecnai G2 F20 for their crystallography and microstructure characterization. PL and Raman spectra were acquired at room temperature with a Jobin Yvon LabRAM HR800 spectrometer equipped with 325 and 532 nm He–Cd lasers as the excitation sources, respectively. The reflectivity spectra were measured using a UV–visible spectrophotometer with a GBC Cintra 10e. The static contact angle measurements were carried out by a contact angle meter with a Digidrop® Model R&D. The surface bonding of SiNWs was characterized by FTIR with a Perkin Elmer spectrum 100. The electrical measurements were carried out with a Keithley 2400.

3. Results and discussion

3.1. Formation of porous SiNW arrays on lightly-doped Si substrates

The morphology of the as-prepared solid SiNW arrays from Si wafers with resistivity of 1–5 Ω cm is shown in Fig. 1a. The NWs, with an average diameter and length of around 80 nm and 13 μm, respectively, show tapered morphology vertically aligned on the substrate. The high-magnification scanning electron microscopy (SEM) image in the inset shows the smooth surface of a NW. Fig. 1b–d are SEM images of porous Si NW arrays generated by the subsequent electrochemical process for 1, 2 and 3 min, respectively. The average lengths of the NWs remain 13 μm, and are not influenced by the electrochemical treatments. From the high-magnification image shown in each inset, the surface of NWs becomes rougher with increasing the duration of electrochemical treatment. Notably, obvious porous structures are seen on the surface of NWs in the inset of Fig. 1d. Apart from some degree of aggregation, the length and morphology of the NWs remain similar after the electrochemical process.

To clearly examine the porous structures, the NWs were characterized by high-resolution transmission electron microscopy (TEM). Fig. 2a–c are bright-field images of single SiNWs prepared by the electrochemical processes for 1, 2 and 3 min, respectively. It shows that the porosity increases with the duration of electrochemical treatment. The average size of pores increases from 1 to 5 nm as the electrochemical duration increases from 1 to 3 min. The nanopores are randomly distributed in the NWs without a specific etching trajectory. Fig. 2d is the electron diffraction pattern of the entire porous SiNW shown in Fig. 2c. It shows that the NW is a single-crystalline structure growing along the [1 0 0] direction. Obviously, the electrochemical etching process did not destroy the crystalline structure of the NW.

3.2. Optical properties of porous SiNWs arrays

The luminescence of porous Si in the visible range has been widely investigated [12] over the previous decade. In this work, photoluminescence (PL) spectra were used to study the effects of electrochemical treatments on the luminescence properties of the SiNWs. As shown in Fig. 3a, the as-prepared solid NWs do not show any obvious peak in the visible range. The NWs treated with electrochemical etching for 1 and 2 min also show similar results. It is notable that when the electrochemical duration is increased to 3 min, the NWs demonstrate a strong broad visible emission centered at 680 nm. Visible emissions in porous Si are generally ascribed to several causes, such as the quantum confinement effect in crystalline Si [9], hydrogenated amorphous silicon [13], surface hydrides [14] or defects in amorphous Si [15]. To examine the surface bonding of the NWs, Fourier transform infrared spectroscopy (FTIR)

Download English Version:

https://daneshyari.com/en/article/10620457

Download Persian Version:

https://daneshyari.com/article/10620457

Daneshyari.com