Microporous and Mesoporous Materials 227 (2016) 152–160

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

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

Optimizing of porous silicon morphology for synthesis of silver nanoparticles

J. Hayder Adawyia, M. Alwan Alwan, A. Jabbar Allaa*

Nanotechnology and Advanced Materials Research Center, University of Technology, Baghdad, Iraq

ARTICLE INFO

Article history:
Received 15 December 2015
Received in revised form
6 February 2016
Accepted 17 February 2016
Available online 20 February 2016

Keywords:
Porous silicon
Surface morphology
Silver nanoparticles
Immersion plating

ABSTRACT

A group of porous silicon (PSi) samples with different surface morphologies prepared at different etching current densities were investigated as a substrate for formation of silver nanoparticles (AgNPs). Simple dipping process of PSi in silver nitrite ($AgNO_3$) with concentrations of 10^{-3}, 10^{-2}, and 5×10^{-2} M was employed to synthesize AgNPs.

The p-type PSi was prepared by electrochemical etching process at different values of current densities. Three different forms of PSi morphology; meso, macro, and pillar with different roughness values 1.21, 177, 89.5, and 38.7 nm were prepared with varying the current densities 30, 60, 90, and 120 mA/cm^2 respectively. The structural and surface morphology properties of samples before and after dipping in $AgNO_3$ were studied through analyzing of scanning electron microscopy (SEM), atomic force microscopy (AFM), and X-ray diffraction (XRD). The results show that the AgNPs sizes depend on the surface morphology and roughness of PSi. The AgNPs prepared by dipping process does not depend on the porosity of the porous layer. For meso pore-like structures the sizes of AgNPs were in the range from 0.52 to 4.09 μm for a low surface roughness, and from 0.52 to 6.83 nm for high surface roughness. For the case of macro pore-like structure which possesses the highest pore sizes and surface roughness, the AgNPs sizes vary from 0.61 to 3.42 μm. The minimum AgNPs size of about 190 nm was obtained from porous surface of pillar form.

1. Introduction

Porous silicon (PSi) was discovered more than 60 years ago [1]. PSi has several unique features. Among its most important features are its very large specific area, which can reach 900 m^2 cm^{-3} [2]. The nature of the chemical surface, porous construction, as well as the semiconducting properties of PSi make it a good supportive material for catalytic applications [3]. Electrochemical etching of silicon in hydro fluoride (HF) containing electrolytes leads to pore formation for a low values of current density and to electro polishing for high applied current density. The converting between pore creations and polishing is accompanied by variation of the surface morphology of etched surface. The etching rate at the boundary between the semiconductor and the electrolyte is determined by the current density. Most of applications rely on the morphology of porous silicon [4,5].

The morphology of the non-dissolved silicon region depends on the etching current density. In the electro polishing phase the silicon surface is etched layer by layer and remains principally flat, while in the porous silicon phase several holes are formed of a size ranging from a few nanometers to microns. Porosities up to 95% relative to crystalline silicon can be reached. The value of the current density during formation of PSi can be up to 120 mA/cm^2, depending on the desired pore size and the fluoride concentration. At current density higher than 120, potential electro polishing will occur. The surface roughness of the porous layer is maintained within an acceptable or desired level of roughness value. The invention also provides an apparatus including a container having an etching solution [6].

The Si–H terminated group and its location on the surface of PSi or the roughness surface are capable of reducing metal ions without adding any reducing agent [7]. Metallic nanoparticles

* Corresponding author.
E-mail address: allaabaldawi2015@gmail.com (A.J. Allaa).

http://dx.doi.org/10.1016/j.micromeso.2016.02.035
1387-1811/

deposition in/on PSi substrate is of particular importance owing to its chemical and biological applications. AgNPs have been interesting researchers due to their unique physical, chemical and biological properties. AgNPs have a high electrical and thermal conductivity, surface-enhanced Raman scattering, chemical stability, catalytic activity and nonlinear optical manners. The distinctive properties of NPs have been employed in wide range of potential applications in medicine, renewable energies, cosmetics, and biomedical devices [8].

The effect of pore sizes in the n-type macro porous structure on the surface morphology of the AgNPs was studied extensively by Ref. [9], and reached to the fact that the large size of individual pore in the range from 400 nm to 1 μm leads to synthesis of a AgNPs inside the pore itself. For meso pore-like structure ranging with pores from 20 nm to 100 nm the ability of PSi to reduce silver ions leads to the formation of nanosized silver particles that have partially merged to form macro sizes of silver particles on PSi surface, with almost no penetration of the metal into the pores [10,11]. A patterned silver structure was formed on a silicon nanoporous pillar array by dipping process, and a composed of sub-micron silver particles arranged around the porous silicon pillars [12].

In this work, we investigated the effects of both of the different forms of p-type porous surface morphology with variable value of surface roughness on the formation and preparation mechanism of AgNPs via silver ion reduction process reaching the optimum condition and controlling the AgNPs. The surface morphologies of as-prepared and AgNPs were examined by SEM, AFM, and XRD analysis.

2. Experimental section

2.1. Chemical materials

Hydrofluoric acid 48%, (CDH), India, was employed as received and diluted with absolute ethanol 99.8%, (SIGMA-ALDRICH, Germany) to create the wanted concentrations of the etching solutions 24% HF. $AgNO_3$ (Aldrich, 99.99%) was dissolved in deionized water to prepare solutions of 10^{-3} M, 10^{-2} M, and 5×10^{-2} M.

2.2. Porous silicon formation

Boron-doped single crystal silicon wafer of (100) orientation with (10 Ω cm) resistivity was used as a substrate for electrochemical etching process. The wafer was divided into small parts 1.5 cm × 1.5 cm. The wafer surface was cleaned using suitable solutions. The porous samples were prepared using electrochemical etching cell [13]. Etching was carried out using a lab-made single cell tank with a Platinum (Pt) wire cathode and an aluminum plate to form the ohmic contact between silicon and power source. The cell consists of Teflon which is resistive against attack from the HF electrolyte. The silicon wafer acts as the anode and it was inserted between the top and the bottom portions of the Teflon. The cathode was a circular Pt ring; immersed in HF electrolyte. The cathode was held in place by the top part of the Teflon cell and plastic ring. The hydrofluoric acid electrolyte was placed inside the top part of the Teflon cell.

Enough electrolytes must be obtainable to provide the necessary fluorine ions and to cover the Pt cathode. The etching current density values were (30, 60, 90, and 120 mA/cm^2) with etching current time of 15 min. The top part of the etching cell has a 1 cm^2 area circular window, which exposes the silicon to HF acid to form the porous silicon. The typical electrochemical etching apparatus is schematically shown in Fig. 1.

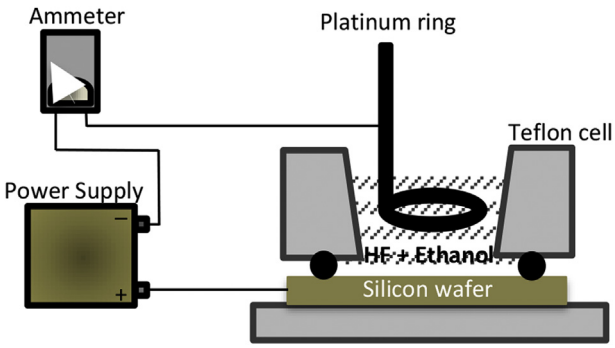

Fig. 1. Schematic diagram of the electrochemical etching system.

2.3. Preparation of AgNPs filled in porous silicon matrix

Fresh PSi substrates were prepared by electrochemical etching, after being immersed in aqueous solution $AgNO_3$ for 10 min to prepare Ag/PSi. The $AgNO_3$ solution concentration was of 10^{-3} M, 10^{-2} M, and 5×10^{-2} M and the dipping process was performed at 25 °C. The morphology of the PSi substrate showed an effected microstructure of the Ag deposits.

2.4. Characterizations

The crystal structure of Ag/PSi was characterized by the experiments of X-ray diffraction (XRD-6000, Shemadzue) whereas the morphology of PSi and Ag/PSi was examined by a scanning electron microscope (SEM, Tescan VEGA 3 SB), Atomic Force Microscopy (AFM) technique in contact mode using the Seiko instrument SPA 400 AFM system. Image-J software was used to calculate pore size and AgNPs size distribution from SEM images.

3. Results and discussion

3.1. Morphological properties of as prepared PSi layer

Fig. 2 shows the effects of etching current density on PSi morphology. The SEM images of the PSi surface of current density of 30, 60, 90, and 120 mA/cm^2 and 15 min etching time are presented. Based on the values of the etching current density and the analysis of SEM images there are three types of PSi morphology:

a Formation of meso porous silicon layer.

The meso porous layer has been formatted on the silicon layer by using electrochemical etching process at etching current density of about 30 mA/cm^2 and etching time of about 15 min in HF solution of concentration of 24%.

b Formation of macro porous layer.

The macro porous layer has been formed on the silicon substrate at etching current density 60 mA/cm^2 with etching time of about 15 min.

c Formation of pillar-porous silicon.

The pillar-form porous silicon was fabricated based on the functionalization of the current density in the range from 90 to 110 mA/cm^2 and etching time of about 15 min.