Microelectronic Engineering 159 (2016) 94–101

Contents lists available at ScienceDirect

Microelectronic Engineering

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

# Investigation of morphology, reflectance and photocatalytic activity of nanostructured silicon surfaces

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ARTICLE INFO

*Article history:*
Received 21 October 2015
Received in revised form 11 February 2016
Accepted 25 February 2016
Available online 5 March 2016

*Keywords:*
Silicon nanostructures
Chemical etching
Morphology
Reflectance
Photocatalysis

ABSTRACT

One-step metal-assisted electroless chemical etching of silicon substrate in aqueous $NH_4F/AgNO_3/HNO_3$ solution is investigated. The effects of etching time and $AgNO_3$ concentration on the morphology and reflectance of etched layer are studied. It is found that the morphology and reflectance depend strongly on these parameters. The lowest reflectance is obtained for 0.009–0.01 Ω·cm p-Si(100) etched in 2 M $NH_4F$–1.89 M $HNO_3$–0.01 M $AgNO_3$ aqueous solution for 15 min. Indeed, the reflectance did not exceed the value of 0.63% in the 200–800 nm range. In addition, nanostructured silicon surfaces obtained through etching using this solution are decorated with copper and silver nanoparticles and their photocatalytic activity for the degradation of rhodamine B under UV and visible light irradiation is evaluated. The highest catalytic activity is observed for samples decorated with Cu nanoparticles. This is attributed to their ability to facilitate electron–hole separation and to promote electron transfer in the photocatalytic process.

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## 1. Introduction

Nanostructured layers on silicon substrates are commonly formed by anodic (electrochemical) or stain etching in hydrofluoric acid (HF)-based solutions [1,2]. While anodization is the most commonly used technique, metal-assisted chemical etching (MACE) has intensively been studied in the last few years. This method allows fabricating various desired silicon nanostructures by choosing different morphologies of catalyst, adjusting the etchant composition or concentration, changing the doping species and level of the silicon substrate, or introducing extra physical fields [3]. It is a purely solution-based, simple and high-throughput technique. It consists of nucleation of metal nanoparticles and anisotropic etching in a solution containing HF and oxidant agents [4–6]. Two different approaches can be envisaged. Indeed, it is a one-step reaction that consists of substrate immersion in a solution containing HF and metal salts (such as $AgNO_3$, $KAuCl_4$…). In this process, the metal deposition and etching are carried out at the same time. The other approach relies on a two-step reaction that involves pre-deposition of metal nanoparticles followed by chemical etching in the presence of HF and an oxidizing agent such as hydrogen peroxide ($H_2O_2$), nitric acid ($HNO_3$) or sodium persulfate ($Na_2S_2O_8$) [4–9]. It is well known that HF is the most common etchant used in MACE of silicon [10–16]. To widen the scope of the chemical etching process, other fluoride-based etchants have been used recently by several groups with the aim to gain a better control over the morphology and properties. Indeed, Brahiti et al. investigated the MACE of silicon in a chemical solution containing an ammonium salt ($NH_4HF_2$) and $AgNO_3$ [17]. It was found that the morphology of etched layer was dependent on the etching temperature, $NH_4HF_2$ concentration and the metal type. Ye et al. used $NH_4F$–$AgNO_3$ system for simultaneous deposition of silver dendrites and formation of a thin porous silicon (por-Si) layer with homogeneous pits [18]. In addition, they demonstrated that the film of silver dendrites on por-Si is an active substrate for enhanced surface-enhanced Raman scattering (SERS) signals of rhodamine B (RhB). Nguyen et al. studied silicon dissolution in $NaBF_4/AgNO_3$ aqueous solution to generate nanostructured Si surfaces with antireflective properties [19]. Another reason for which the research is oriented towards the development of new chemical etching solutions is to obtain somewhat particular morphologies that allow improving the performance of some analysis methods. Indeed, we have recently demonstrated that nanostructured silicon substrates, easily prepared by chemical etching of crystalline silicon in $NH_4F/HNO_3/AgNO_3$ aqueous solution, can be used as new targets for matrix-free laser desorption ionization-mass spectrometry (LDI-MS) analysis [20,21]. These samples that are composed of two nanostructured layers were the most efficient in terms of signal intensities and number of detected peptides as compared to silicon nanowires prepared by the vapor–liquid-solid growth mechanism or a commercial NADLI surface. They allowed soft desorption/ionization of a large variety of peptides with masses ranging from 380 to 1700 Da. These studies were limited only to evaluate the LDI-

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http://dx.doi.org/10.1016/j.mee.2016.02.060
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MS performance of the nanostructured substrates, fabricated by MACE method in a new chemical aqueous solution, $NH_4F/HNO_3/AgNO_3$. However, Megouda et al. studied, using the same aqueous solution, the influence of silicon type, doping level and crystallographic orientation on the morphology and antireflective properties [22].

In continuation of our investigations on MACE of silicon, the present work is devoted to study the influence of etching time and $AgNO_3$ concentration on the morphology and anti-reflective properties of the etched layers. We show that a reflectance lower than 1% in the range of 200–800 nm can be achieved, which is lower than that obtained in our previous work [22]. In addition, nanostructured silicon surfaces decorated with Cu and Ag nanoparticles are examined for the photodegradation of RhB under UV and visible light irradiation. The degradation process of RhB was followed by UV–vis spectrophotometry by monitoring the decrease of the absorption peak at 555 nm. The highest catalytic activity was found for samples decorated with Cu nanoparticles under UV irradiation with a full degradation after 60 min.

## 2. Experimental part

### 2.1. Chemicals and reagents

All cleaning and etching reagents used for the preparation of the silicon nanostructures such as acetone, isopropyl alcohol (i-PrOH), ammonium fluoride ($NH_4F$, 40%, pH 8), sulfuric acid ($H_2SO_4$, 96%) and hydrogen peroxide ($H_2O_2$, 30%) were clean room grade (VLSI) and purchased from Carlo Erba. All other chemicals were reagent grade or higher and were used as received unless otherwise specified. Nitric acid ($HNO_3$, 65%), acetic acid ($CH_3COOH$) and hydrochloric acid (HCl, 37%) were purchased from Merck. Silver nitrate ($AgNO_3$) was obtained from Sigma-Aldrich.

Deionized water used in all the experiments was obtained using a Milli-Q system (Millipore, Milford, USA).

### 2.2. Sample preparation

1. Preparation of nanostructured silicon substrates (NSi)
   p-Si(100) (0.009–0.01 Ω·cm) wafers used in this study were obtained from Sil'tronix-ST, Archamps, France. The silicon surface was first degreased in acetone and isopropanol, rinsed with Milli-Q water, and then cleaned in a piranha solution (3:1 concentrated $H_2SO_4$/30% $H_2O_2$) for 20 min at 80 °C, followed by copious rinsing with Milli-Q water. The nanostructured silicon surfaces were obtained by chemical etching of the clean substrate in $NH_4F/HNO_3/AgNO_3$ (2 M/1.89 M/x M) aqueous solution at room temperature. The experimental values of x are 0.01, 0.02 and 0.03. For $AgNO_3$ concentration of 0.02 M, the etching time was varied from 5 to 20 min by a step of 5 min. For $AgNO_3$ concentrations of 0.01 M and 0.03 M, the etching time was maintained constant at 10 min. The resulting surfaces were rinsed copiously with deionized water and immersed in an aqueous solution of $HCl/HNO_3/H_2O$ (1/1/1) overnight at room temperature to remove the silver nanoparticles and dendrites deposited on the surface during the chemical etching.
2. Preparation of silver nanoparticle–silicon nanostructures (Ag NP–NSi)
   Silver nanoparticles were deposited on nanostructured silicon surface by dipping the sample into two different aqueous solutions: 0.005 M HF–2.75 M $AgNO_3$ (Ag1) and 2.31 M HF–0.02 M $AgNO_3$ (Ag2) at ambient temperature for 2 min. The resulting surfaces were rinsed with water and dried under a gentle stream of nitrogen.
3. Preparation of copper nanoparticle–silicon nanowire arrays (Cu NP–NSi)
   Copper nanoparticles were deposited on a nanostructured silicon surface at ambient temperature by dipping the sample into two different aqueous solutions: 1.45 M HF–0.035 M $CuCl_2$ for 1 min (Cu1) and 1.35 M HF–0.14 M $CuCl_2$ for 2 min (Cu2). The resulting surfaces were rinsed with water and dried under a gentle stream of nitrogen.

### 2.3. Photocatalytic degradation of rhodamine B

Rhodamine B was used as the model of organic pollutant to evaluate the photocatalytic activity of the nanostructured silicon samples. Nanostructured silicon samples (1.2 cm × 0.8 cm) were immersed into RhB aqueous solution with an initial concentration of $0.5 \cdot 10^{-5}$ mol·L$^{-1}$. The samples were irradiated with UV ($\lambda = 365$ nm) or visible light ($\lambda > 420$ nm). The experiments were performed at room temperature for 2 h. Each 20 min, the concentration of RhB was determined using a UV–vis spectrophotometer by monitoring the absorption peak at 555 nm. The RhB irradiation was carried out under different conditions:

(i) Direct irradiation without sample.
(ii) In the presence of hydrogen-terminated silicon substrate (H–Si).
(iii) In the presence of hydrogen-terminated nanostructured silicon (H–NSi).
(iv) In the presence of oxidized nanostructured silicon (O–NSi).
(v) In the presence of nanostructured silicon coated with Ag nanoparticles (Ag–NSi).
(vi) In the presence of nanostructured silicon coated with Cu nanoparticles (Cu–NSi).

### 2.4. Surface characterization

1. Scanning Electron Microscopy (SEM)
   Scanning Electron Microscopy (SEM) images were obtained using an electron microscope ULTRA 55 (Zeiss, France) equipped with a thermal field emission emitter and three different detectors (EsB detector with filter grid, high-efficiency In-lens SE detector, Everhart–Thornley secondary electron detector) and an energy dispersive X-ray analysis device (EDX analysis).
2. Reflectance measurements
   The reflectance measurements were performed using a UV–vis spectrophotometer (Perkin-Elmer Lambda UV/Vis 950 spectrophotometer) equipped with an integrating sphere. The scans were measured for wavelengths ranging from 200 to 800 nm at an incident light angle of 45° and at different locations on each scanned surface.
3. UV/Vis measurements
   Absorption spectra were recorded using a Perkin Elmer Lambda UV/Vis 800 spectrophotometer in quartz cuvettes with an optical path of 10 mm. The wavelength range was 400–800 nm.

## 3. Results and discussion

1. Morphology
   In a previous report, we have studied the etching of silicon of different resistivities in $NH_4F/HNO_3/AgNO_3$ solutions [22]. The results showed the formation of an etched film consisting of two nanostructured layers for both n- and p-type silicon of low resistivity in contrast to silicon of high resistivity where only one nanostructured layer was observed. In this work, we study the effect of $AgNO_3$ concentration and etching time on the morphology of low resistivity p-type silicon etched in $NH_4F/HNO_3/AgNO_3$ solution.
   The SEM image in Fig. 1a displays the formation of holes of different shapes reaching sizes around one hundred of nanometers after etching in 2 M $NH_4F$–1.89 M $HNO_3$–0.01 M $AgNO_3$ solution for 10 min. The etching depth is about 200 nm (Fig. 1b). However, increasing the concentration of $AgNO_3$ in the etching solution to 0.02 M results in an increase in hole size to a few hundred nanometers due to the dissolution of the walls between the holes (Fig. 1c). In addition, the hole surface becomes nanoporous. The depth of these holes is about 440 nm as can be seen in a cross section SEM image in

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