Applied Surface Science 258 (2012) 5628–5637

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

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

Metal-assisted electroless etching of silicon in aqueous NH_4HF_2 solution

Naima Brahiti [a], Sihem-Aissiou Bouanik [b], Toufik Hadjersi [b,*]

[a] Département de physique, Faculté des Sciences, Université M'Hamed Bougara, Boumerdes, Algeria
[b] Unité de Développement de la Technologie du Silicium (UDTS), 2, Bd. Frantz Fanon, B.P. 140 Alger-7 Merveilles, Alger, Algeria

ARTICLE INFO

Article history:
Received 17 January 2012
Received in revised form 12 February 2012
Accepted 13 February 2012
Available online 3 March 2012

PACS:
62.23.Hj
68.37.Hk
81.65.cf
82.45.jn

Keywords:
Silicon nanostructures
Silicon nanowires
Metal-assisted electroless etching
Catalyst

ABSTRACT

One-step and two-step metal-assisted electroless chemical etchings of p-type silicon substrate in new solutions were investigated. In the one-step etching process, the etching is performed in $NH_4HF_2/AgNO_3$ solution. On the other hand, the two-step etching process involves chemical deposition of noble metal onto silicon substrate surface followed by electroless etching in NH_4HF_2/H_2O_2 solution. The effect of several parameters on the morphology of etched layer was studied namely: pH of etching solution for the two cases and the etching temperature, the concentration of NH_4HF_2 and the type of metal deposited on silicon surface for second case. It is shown that the morphology depends strongly on etching parameters where different nanostructure shapes can be formed. An important result is that silicon nanowires are formed at pH = 4 and pH ≤ 2 for the first and second case, respectively.

1. Introduction

Recently, silicon nanowires (SiNWs) have received increased interest due to their unique one-dimensional physical morphology and the associated electrical, mechanical, chemical, optoelectronic and thermal properties. These properties make them particularly appealing for the fabrication of various high-performance devices such as batteries, solar cells, detectors, thermoelectric systems [1], biological/chemical sensors [2,3], microfluidics [4–6], and their use as matrix-free laser desorption/ionization mass spectrometry substrates [7,8]. Usually, they are synthesized by different approaches such as: Vapor–Liquid–Solid technique (VLS) [9], laser ablation [10,11], thermal evaporation decomposition [12,13], and other methods were developed [14–16]. However, most of these methods need either high synthesis temperatures or intolerably long synthesis times due to the limitation of the growth mechanisms. Recently, a simple, fast, and effective nanostructures formation method which no needs the lithography technique, named metal-assisted chemical etching, was reported by Peng et al. [17]. It allows obtaining a wide range of silicon nanostructures on a large surface, ranging from nanowires to continuous pore walls or coalescence of multiple wires of different dimensions [18]. In this method the etching is catalysed by metal without external bias and the nanostructures are fabricated unselectively on the whole silicon. It can be classified in two types, one-step reaction in etchant solution containing HF and metal salts (such as $AgNO_3$, $KAuCl_4$) and two-step reaction that involves the predeposition of metal nanoparticles or patterned metal thin films followed by chemical etching in the presence of HF and H_2O_2 [19]. In the first type, the metal deposition and the etching are carried out in the same chemical solution. On the other hand, in the second type they are performed in two different chemical solutions. In both types, the interconnected metallic nanoparticles deposited on the silicon surface catalyse the etching reaction, sink below the surface and leave pores behind. The unetched silicon between pores forms nanowires [19]. This method is broadly studied for the synthesis of silicon nanowires where it is shown that the lengths and morphologies of the SiNW arrays are strongly affected by the etching conditions [20–25]. However, in all studies made up to now, the formation of silicon nanowires is performed only by etching in HF-based solutions. Since the HF is a hazardous acid, it will interest to replace it by another product safer that allows supplying the fluoride in the etching solution as the HF which is necessary for the silicon dissolution. Recently, the ammonium hydrogen difluoride (NH_4HF_2) was used in different processing. Indeed, it is reported that the silicon surfaces treated with NH_4F^- and $NH_4HF_2{}^-$ are highly hydrophobic, indicating the production of clean, hydrogen-terminated surfaces [26]. Moreover, NH_4HF_2, was used as a defect delineating etchant of apophyllite and

* Corresponding author.
E-mail address: hadjersi@yahoo.com (T. Hadjersi).

0169-4332/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2012.02.043

quartz single crystals [27,28]. Thereafter, it was reported by Koker and Kolasinski that HF_2^- etches the silicon ∼15 times faster than HF via photoelectrochemistry [29]. Basing on this result, Nahidi and Kolasinski are decided to study the stain etching of silicon in an untested etchant solution which containing NH_4HF_2 instead of HF [30]. Thus, they discovered a new class of stain etchant composed of NH_4HF_2, HNO_3, and H_2O. They demonstrated that the ratio NH_4HF_2:HNO_3:H_2O is critical. To maintain the efficiency of porous film formation, a balance between oxidation and fluoride-related etching must be maintained. Too little NH_4HF_2 slows down the rate and too much HNO_3 does not produce pores. So far, there is no report on the metal-assisted electroless etching to produce either porous silicon or SiNWs in solution containing NH_4HF_2. The latter has the advantage of being a solid with a positive heat of solution in water that is much easier to handle than fuming concentrated HF [30]. Moreover, it is less hazardous than HF and supply the HF_2^- in etching solution. Motivated by this, we have developed a non-HF based solution which allows obtaining different shapes of silicon nanostructures by the metal-assisted electroless chemical etching process.

In this work, we have investigated the effect of metal-assisted electroless etching parameters in chemical solutions containing NH_4HF_2. The resulting etched layers were investigated by scanning electron microscopy (SEM). We show that the silicon nanowires are only formed at pH = 4 and pH ≤ 2 for one-step and two-step metal-assisted electroless chemical etching method, respectively.

2. Experimental

p-Type Cz-Si (1 0 0) substrates of resistivity 0.5–2 Ω cm were used in this study. The silicon substrates were first cleaned by ultrasonication in trichloroethylene, acetone and deionized water (5 min each), followed by metal-assisted electroless chemical etching. Two sets of samples were prepared. In the first set, the samples were subjected to the one-step Ag-assisted electroless chemical etching in 15 g NH_4HF_2:0.05 M $AgNO_3$:90 cc H_2O. The etching process was studied as a function of the etching solution pH which was changed by adding of HCl drops. The values of pH studied were 1, 3 and 4. After the etching, the samples were found to be covered with a thick Ag layer, which was removed by immersion into aqueous HNO_3 solution during 3 min. In the second set, the metal deposition on silicon surface was carried out before etching in 15 g NH_4HF_2: oxidant agent:H_2O_2 solution. For the case where the etching solution contains H_2O_2 as an oxidant agent, Au, Ag, Pt and Pd were experimented as metallic deposition for which four chemical solutions were prepared:

1. 27.82 M HF:0,05 M $AgNO_3$:H_2O
2. 0.15 M HF:1 mM $PdCl_2$
3. 0.15 M HF:1 mM $AuCl_3$
4. 0.15 M HF:1 mM PtO_2

Ag, Pd and Au were deposited at room temperature in the first, second and third solution, respectively. The deposition time was 30 s for Ag and 10 min for Pd and Au. On the other hand, the Pt was deposited in the fourth solution at 50 °C for 10 min. In the second and fourth solution, 10 cc HCl was added to facilitate the dissolution of $PdCl_2$ and PtO_2, respectively. Prior to metal deposition, the clean samples were immersed in 10% HF aqueous solution for 2 min at room temperature to remove the native oxide.

For each deposited metal type, three samples were prepared where each one was etched in a solution of well determined pH value (1, 2 or 3). In the case of Ag as deposited metal, the effect of etching temperature and type of oxidant agent on the etching process were also studied. In the former case, the etching of two samples was performed at higher temperature (50 °C) in two solutions of pH = 1 and 2. On the other hand, in the second case, the oxidant agent H_2O_2 was replaced by $FeCl_3$ in the etching solution. In this case, two samples were etched after Ag deposition in 15 g NH_4HF_2:0.44 M $FeCl_2$:90 cc H_2O solution of pH = 1 and 2. In addition, in the same set, the concentration of NH_4HF_2 in the etching solution $x$$NH_4HF_2$:40 cc H_2O_2:50 cc H_2O was studied by increasing the value of x from 10 g to 30 g by step of 5 g. Finally, after etching, the samples were rinsed with deionized water and dried under a gentle stream of nitrogen. The etching was performed at room temperature except in the specified cases.

The morphology was examined by scanning electron microscopy (SEM) using a PHILIPS (XL 30) equipped with an energy dispersive X-ray analysis device (EDX analysis).

3. Results and discussion

One-step and two-step metal-assisted electroless chemical etching of p-Si (1 0 0) of resistivity 0.5–2 Ω cm in new solution containing NH_4HF_2 instead of HF were investigated. For each method, the effect of one or several etching parameters on the etched layer morphology was studied.

3.1. One-step metal-assisted electroless chemical etching

The silicon sample was etched in 15 g NH_4HF_2:0.05 M $AgNO_3$:90 cc H_2O solution of pH = 4 at room temperature for 30 min. In order to explore the effect of solution pH on etched layer morphology, two other solutions of lower pH value (pH = 3 and 1) were prepared. The pH was reduced by adding some HCl drops to the aforementioned solution. At naked eyes, it was observed that the samples etched in solution of pH = 1 and 3 have a reflecting surface which indicates that the etching was weak. The observation with

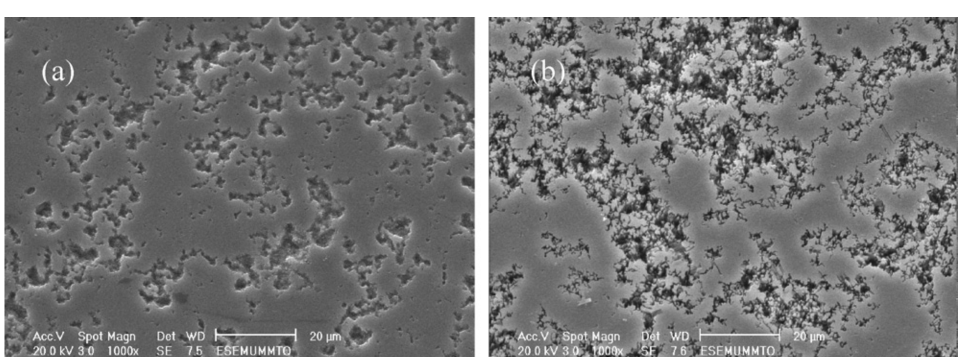

Fig. 1. Plan view SEM images of Ag-assisted electroless etched silicon in 15 g NH_4HF_2:0.05 M $AgNO_3$:90 cc H_2O solution of pH = 1 (a) and pH = 3 (b) at room temperature for 30 min.