Journal of Luminescence 129 (2009) 1750–1753

Contents lists available at ScienceDirect

Journal of Luminescence

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

Formation of aligned silicon nanowire on silicon by electroless etching in HF solution

N. Megouda [a], R. Douani [a], T. Hadjersi [b,*], R. Boukherroub [c]

[a] Faculté des Sciences, Université Mouloud Mammeri, Tizi-Ouzou, Algeria
[b] Unité de Développement de la Technologie du Silicium (UDTS), 2, Bd. Frantz Fanon, B.P. 140 Alger-7 merveilles, Alger, Algeria
[c] Institut de Recherche Interdisciplinaire (IRI, FRE 2963), Institut d'Electronique, de Microélectronique et de Nanotechnologie (IEMN, CNRS-8520), Cité Scientifique, Avenue Poincaré—B.P. 60069, 59652 Villeneuve d'Ascq, France

ARTICLE INFO

Available online 19 May 2009

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

Keywords:
Nanostructures
Silicon nanowires
Electroless etching

ABSTRACT

It was demonstrated that the etching in HF-based aqueous solution containing $AgNO_3$ and $Na_2S_2O_8$ as oxidizing agents or by Au-assisted electroless etching in HF/H_2O_2 solution at 50 °C yields films composed of aligned Si nanowire (SiNW). SiNW of diameters ~10 nm were formed. The morphology and the photoluminescence (PL) of the etched layer as a function of etching solution composition were studied. The SiNW layers formed on silicon were investigated by scanning electron microscopy (SEM), energy-dispersive X-ray (EDX) and photoluminescence. It was demonstrated that the morphology and the photoluminescence of the etched layers strongly depends on the type of etching solution. Finally, a discussion on the formation process of the silicon nanowires is presented.

1. Introduction

Porous silicon has attracted a great deal of attention over the recent years, mainly due to their unique optical properties and their ability to emit visible light at room temperature [1]. The luminescence from porous silicon is particularly interesting, since it allows developing silicon-based optoelectronics devices [2]. It is usually prepared by anodization or stain etching of silicon in aqueous hydrogen fluoride (HF) solutions [3,4]. The stain etching is relatively simple compared to the electrochemical method, since they require no electrodes on the back surface of crystalline Si wafers [4]. However, it provides PL intensities in an order of magnitude smaller than conventional electrochemically etched PS [5]. Recently, we have used a new metal-assisted electroless etching method [6], developed previously by Li and Bohn [7] to produce visible-light-emitting layers. It needs no electrodes on the back surface of silicon wafers and enables formation of uniform porous silicon layers. A thin metallic film (Au, Pt, Al, Pd …) is generally deposited directly on a silicon surface prior to immersion in an etchant composed of HF and an oxidizing agent. Upon irradiation with ultraviolet light, porous silicon emits in the visible spectral range, and the peak emission wavelength can be tuned simply by varying the time of etching [8]. It is well known that in the process of metal-assisted electroless etching, the metal nanoparticles, which are deposited onto the substrate surface, catalyze the etching reaction, sink below the surface and leave behind pores [9]. According to the literature, the shape of the generated pores depends on several etching parameters such as the shape of the metal particle, the concentration of HF and the type of oxidant agent used in the etching solution [9,10]. Tsujino et al. assumed that the shape of the generated pore and the Ag-particle were related [11]. They considered that nonspherical Ag particles change etching course in the crystallographically identical ⟨1 0 0⟩ directions giving non-straight pores contrary to what was observed for spherical Ag particles. The same authors also noted that the etching was faster when the sample was loaded with Pt particles instead of Ag particles [10]. This was attributed to the fact that more positive holes were injected into Si when Pt particles were used. Peng et al. observed during etching in $HF/Fe(NO_3)_3$ that the pores generated with stable Pt particles were not as straight as those obtained with Ag and Au particles [12]. They also showed that the etching in $HF/AgNO_3$ solutions yields films composed of aligned Si nanowire (SiNW) [13]. Recently, we showed that cylindrical pores were also formed in $HF/K_2Cr_2O_7$ solution [9]. On the other hand, in $HF/Na_2S_2O_8$ solution randomly propagating pores and winding pores were formed in and under the microporous layer, respectively [9]. Li and Bohn have shown that the Au-electroless etched silicon in 1:1:1 EtOH:HF(49%):H_2O_2(30%) solution exhibits columnar structure [7].

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

0022-2313/$ - see front matter © 2009 Published by Elsevier B.V.
doi:10.1016/j.jlumin.2009.04.094

In this work, we shown that the etching in HF/($AgNO_3$+$Na_2S_2O_8$) or by Au-assisted electroless etching in HF/H_2O_2 solution yields films composed of aligned Si nanowire. A comparative study of the morphologies and luminescence properties of etched layers obtained by these two methods was made. The layers formed on silicon were investigated by scanning electron microscopy (SEM) and photoluminescence (PL) measurements.

2. Experimental procedure

The Au-assisted chemical etching processes were applied to p-type, Cz-grown, Si (1 0 0) wafers with a resistivity of 100 Ω cm. Thin gold films of approximately 4 nm were sputtered onto the silicon samples. After rinsing with deionised water of the metal-deposited samples, the samples were immersed in a solution of 26.35 M HF-0.89 M H_2O_2–H_2O for etching. Then, the samples were rinsed with deionised water. The etching was performed at 50 °C for 10 min. Some other samples were etched in HF/($AgNO_3$+$Na_2S_2O_8$) solution for 1 h at 50 °C. The concentration of hydrofluoric acid (HF) and silver nitrate ($AgNO_3$) were kept at 22.5 M and 0.05 M, respectively. The sodium persulfate $Na_2S_2O_8$ concentration was of 0.025 M. The thick silver film wrapping the silicon wafer was etched away before microstructural observation.

The scanning electron microscopy observations were performed using a Philips XL 30 microscope. Photoluminescence from the chemically etched silicon was measured under wavelength excitation of 325 nm using a Perkin-Elmer LS50B luminescence spectrometer with a scan rate of 300 nm/min. The measurements were performed at room temperature.

3. Results and discussion

Fig. 1 displays a plan view SEM image of a p-Si sample which was subjected to etching in HF/(0.05 M $AgNO_3$+0.025 M $Na_2S_2O_8$) solution for 1 h at 50 °C. It can be seen that the surface is wrapped by dendrites. The energy-dispersive X-ray (EDX) spectroscopy showed that these dendrites are composed of silver (Fig. 2). After removing the silver dendrite films from the surface, silicon nanowires with diameters of about 100 nm were observed (Fig. 3). Also, it can be seen that large quantities of well-aligned silicon nanowire were produced. EDX analysis (not presented here) shows that the silicon is the main component of these

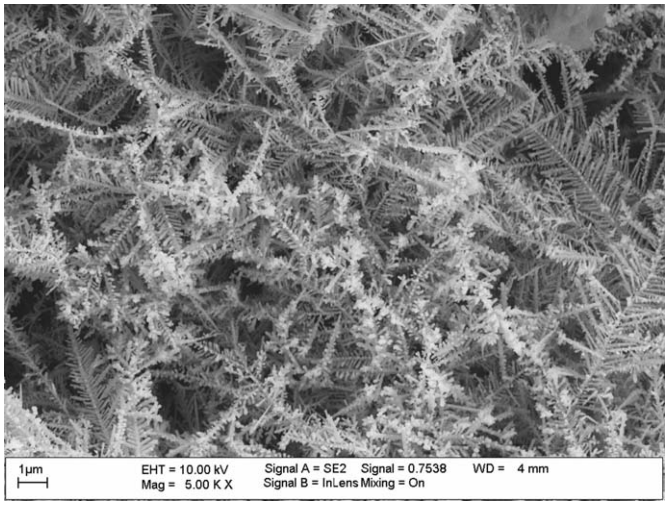

Fig. 1. SEM image of branched silver dendrites formed on Si sample after etching in HF/$AgNO_3$/$Na_2S_2O_8$ solution at 50 °C for 60 min.

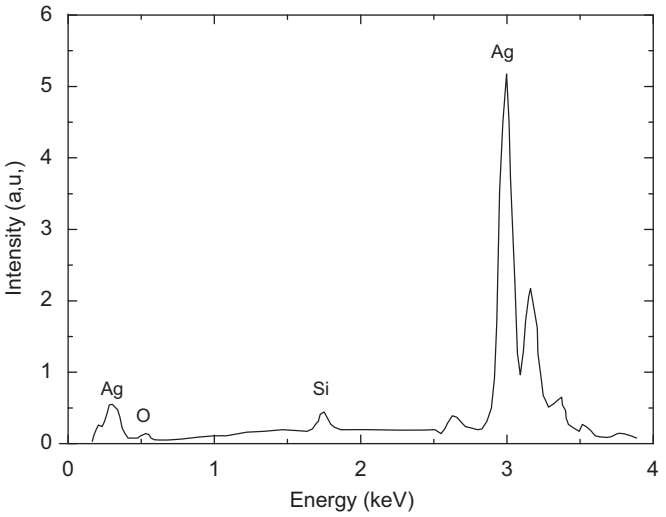

Fig. 2. Energy-dispersive X-ray spectrum of silver dendrites formed on Si sample by etching in HF/$Na_2S_2O_8$/$AgNO_3$ solution at 50 °C for 60 min.

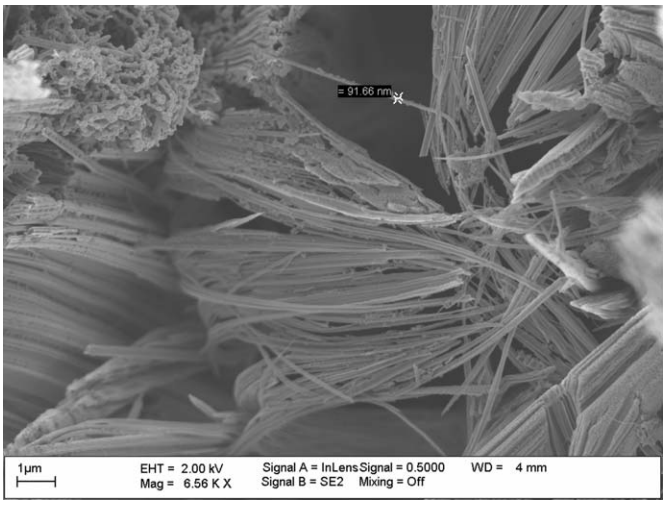

Fig. 3. Plan view SEM image of silicon nanowires formed by etching in HF/$AgNO_3$/$Na_2S_2O_8$ solution at 50 °C for 60 min.

nanowires. A cross-sectional view shows that the etched layer is composed of well-aligned nanowires perpendicular to surface of the sample (Fig. 4). Their length is about 120 μm (i.e. the etched depth). The interface between substrate and etched layer is rough. This structure is similar to that obtained by K.Q. Peng et al. using a two-step process: electroless deposition of a Ag-nanoparticle film in HF/$AgNO_3$ solution followed by chemical etching in HF/$Fe(NO_3)_3$ solution at 50 °C [12]. Also, T. Qiu et al. prepared almost the same structure by etching in HF/$AgNO_3$ solution at 50 °C [14]. A different morphology is obtained when a p-Si(1 0 0) sample was Au-assisted electroless etched in HF/H_2O_2 solution for 10 min at 50 °C as can be observed in Fig. 5a. Indeed, it shows that the density of silicon nanowires is not high as in the previous case, since they are formed in islands separated by macroporous regions. This is well shown on cross-sectional view SEM image (Fig. 6). Indeed, it can be observed that the top layer is composed of well-aligned nanowires as macropores perpendicular to sample surface. The thickness of the top layer is about 3.7 μm. The diameter of nanowires is about 10 nm (Fig. 5b). The region under top layer which can reach a depth of about 35 μm is dominated by macropores that propagate randomly. It is important to note this