



# Chemical wet etching of germanium assisted with catalytic-metal-particles and electroless-metal-deposition



Kazuki Ito\*, Daichi Yamaura, Toshio Ogino

Graduate School of Engineering, Yokohama National University, Tokiwadai 79-5, Hodogaya-ku, Yokohama 240-8501, Japan

## ARTICLE INFO

### Article history:

Received 23 February 2016

Received in revised form 2 August 2016

Accepted 4 August 2016

Available online 4 August 2016

### Keywords:

Germanium

Wet etching

Lithium ion battery

Surface structure

Nano-structure

## ABSTRACT

Ge nanostructures were fabricated by wet processes based on etching assisted with the catalytic-metal-particles and the electroless-metal-deposition under various conditions. In the etching assisted with catalytic-metal-particles, we used HF + H<sub>2</sub>O<sub>2</sub> solutions after forming Ag particles on the Ge wafer surfaces from an AgNO<sub>3</sub> solution. We succeeded in fabrication of porous layers on the Ge substrates and found that the pore sidewall inclination angles with respect to the surfaces can be controlled by the H<sub>2</sub>O<sub>2</sub> concentrations. In the etching assisted with electroless-metal-deposition, we fabricated whisker-like nanostructures and demonstrated that their size and morphology can be varied by changing the AgNO<sub>3</sub> concentration, deposition/etching time and the substrate resistivity. We have revealed differences between Ge and Si in the metal-catalyzed etching and pointed out problems in Ge nanowire fabrication via a wet chemical etching.

© 2016 Elsevier Ltd. All rights reserved.

## 1. Introduction

Lithium ion batteries (LIBs) are widely used in various electronic devices and vehicles owing to their outstanding characteristics, such as long lifetime, high voltage and high energy density. As an anode material, graphite with a maximum Li<sup>+</sup> charge capacity of 372 mAh/g are commercially used [1,2]. Towards realization of further high capacity, new anode materials, such as silicon (Si) and germanium (Ge), attract much attention. In particular, Si exhibits higher Li<sup>+</sup> storage capacity of about 4,200 mAh/g [3] than graphite. However, Si volume expands by about 400% during lithiation [4], which causes structural destruction of the Si anodes, resulting in rapid degradation of the battery capacity. To solve this problem, nanostructuring of the Si anodes has been intensively studied. Si nanowire is one of the promising candidates to relax the anode material destruction. Concerning Si nanowire formation, various methods, such as vapor-liquid-solid (VLS) growth [5–7] and wet chemical etching method [8–10] have been reported. Among them, wet chemical etching is well known as a simple, less-expensive method.

Ge also has a high specific capacity of 1,600 mAh/g, and its electrical conductivity and Li<sup>+</sup> diffusion coefficient are 10,000 times and 400 times higher than those of Si, respectively [11,12].

These characteristics are advantageous to the high-rate cycle performance, whereas Si does not exhibit it [13]. Ge, however, is also accompanied with a large volume expansion of ~370% for Li<sup>+</sup> incorporation in the charging process [14]. This volume expansion also would cause destruction of the Ge anodes. As well as Si nanostructure for anodes, Ge nanostructures with free spaces around them could relax the stress caused by the volume expansion. Therefore, nanostructuring of Ge anodes is also required for long lifetime batteries. Up to now, nanowire formation using the VLS growth mode have been reported [15]. But, fabrication of Ge nanowires using VLS growth requires use of dangerous gas, GeH<sub>4</sub>, so we should develop an easy, safe process. Wet etching is a safe, simple and less-expensive method to fabricate Ge nanostructures. Nevertheless, there have been few reports about Ge nanostructure fabrication using wet etching, and the mechanism of Ge wet etching has not been elucidated. T. Kawase et al. [16,17] formed inverted pyramid pits on Ge surfaces using metal-assisted chemical etching. M. Aizawa et al. [18] found that many pits formed on Ge surfaces through a process similar to the electroless deposition. However, no study has been reported on Ge nanowires formation using the wet chemical etching assisted with catalytic-metal-particles or electroless-metal-deposition.

In this work, we fabricated Ge nanostructures using chemical wet etching of Ge assisted with catalytic-metal-particles and electroless-metal-deposition under various conditions. In the former method, the metal particles catalyze the Ge etching in an etchant, and, in the latter one, Ge etching occurs simultaneously

\* Corresponding author.

E-mail address: [ito-kazuki-xc@ynu.jp](mailto:ito-kazuki-xc@ynu.jp) (K. Ito).

**Table 1**  
Summary of the etching conditions.

experimental item	AgNO <sub>3</sub> concentration (mM)	etching time (h)	Resistivity (Ωcm)
#1	0.01 0.025 0.05	20, 46, 66	0.23–0.25
#2	0.05	20	0.01–0.1 0.23–0.25

with electroless-metal-deposition via an electron transfer from Ge to the deposited metal surfaces. Based on understanding of the etching mechanisms, we propose formation models of various Ge nanostructures.

## 2. Experiments

### 2.1. Chemical wet etching of Ge assisted with catalytic-metal-particles

We used p-type Ge(100) substrates with resistivity of 0.01–0.1 Ωcm. The wafers were ultrasonically washed in acetone and ethanol for 5 min each to remove organic contaminants, and the oxide layers on the surfaces were removed by rinsing with deionized water for 5 min. Ag particles were deposited by immersing the Ge substrates in a 5 mM AgNO<sub>3</sub> solution for 1 min. Then, the wafers were immersed in the etchant consisting of HF and H<sub>2</sub>O<sub>2</sub> solutions. The HF concentration of the etchant was fixed to be 5 M, whereas the H<sub>2</sub>O<sub>2</sub> concentration was varied to be 0.1 M, 0.3 M and 0.6 M. The etching time was 1 hour. After the etching, the Ag layers on the surfaces were dissolved with a HNO<sub>3</sub> solution and rinsed with deionized water. The sample surface morphology was observed by scanning electron microscopy (SEM, HITACHI S-4700).

### 2.2. Chemical wet etching of Ge assisted with electroless-metal-deposition

In this etching mode, we used p-type Ge(100) substrates. The organic contaminants and the oxide layers were removed with the

same procedure as that described in 2.1. Next, the substrates were dipped into low-concentration AgNO<sub>3</sub> solutions. The used AgNO<sub>3</sub> concentrations, etching times, and resistivity of the substrates are summarized in Table 1. Then, silver dendrites on the surfaces were dissolved with HNO<sub>3</sub> solution. The substrates were rinsed and observed by SEM.

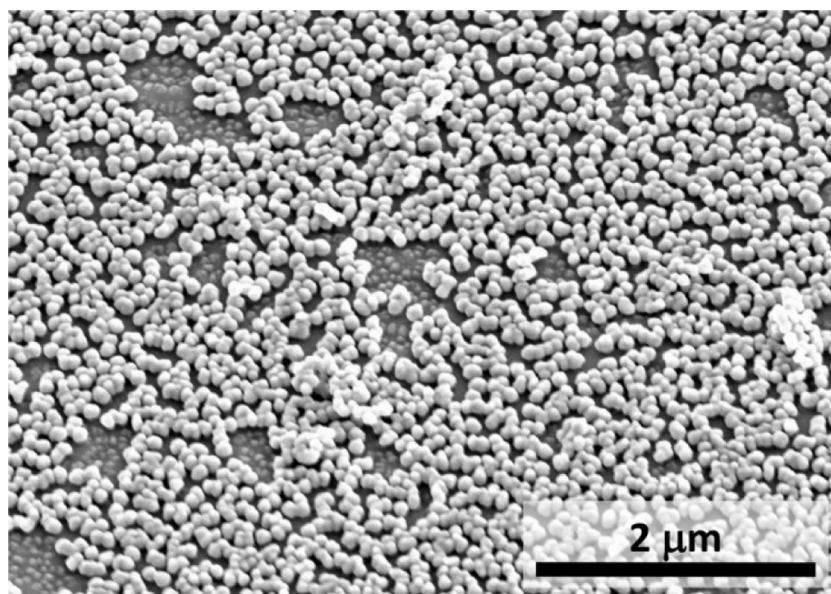
## 3. Results

### 3.1. Chemical wet etching of Ge assisted with catalytic-metal-particles

After the Ag deposition process, it was observed that the whole substrate surfaces were covered with Ag nanoparticles of about 100 nm in diameter, as shown in Fig. 1. Fig. 2 shows SEM images of the etched Ge surfaces (a–c) with and (d–f) without the Ag particles, respectively, using the etchants of (a,d) 5 M-HF + 0.1-M H<sub>2</sub>O<sub>2</sub>, (b,e) 5-M HF + 0.3-M H<sub>2</sub>O<sub>2</sub> and (c,f) 5-M HF + 0.6-M H<sub>2</sub>O<sub>2</sub>, respectively. In Fig. 2a, the Ag particles are distributed on the whole areas including the ridges as well as the bottoms of the microscaled structures. In Fig. 2b and c, almost whole Ag particles form clusters and are located in the bottom areas of the microstructures. In Fig. 2d, nanoscaled pores perpendicular to the surface are observed in addition to microscaled crater-like pores. In Fig. 2e, nanopore is not observed, and openings of the microscaled craters are extended compared with Fig. 2d. However, high density ridges similar to those in Fig. 2d remain on the microscaled crater walls. In Fig. 2f, the nanoscaled morphology, such as nanopores and nanoridges, disappeared, and only microscaled crater-like pores with smooth side walls remained on the etched surface.

In comparison with Fig. 2(a–c) and Fig. 2(d–e), morphological changes of Ge structures were not observed except for with or without Ag particles on the Ge substrate, so we think that there is no, at least negligible effect of HNO<sub>3</sub> solution on morphology of the Ge substrate during the Ag etching.

Fig. 3 shows the opening diameter distributions of the pores formed by the different H<sub>2</sub>O<sub>2</sub> concentrations. As the H<sub>2</sub>O<sub>2</sub> concentration increases, the pore diameter at the openings becomes larger. In the result of 0.1-M H<sub>2</sub>O<sub>2</sub> concentration shown in the black line indicates that the pore size is classified into two



**Fig. 1.** SEM image of Ag particles deposited on a Ge substrate before the Ge etching.

Download English Version:

<https://daneshyari.com/en/article/4767736>

Download Persian Version:

<https://daneshyari.com/article/4767736>

[Daneshyari.com](https://daneshyari.com)