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

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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 + H₂O₂ solutions after forming Ag particles on the Ge wafer surfaces from an AgNO₃ 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 H₂O₂ 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 AgNO₃ 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.

Keywords

Germanium; Wet etching; Lithium Ion Battery; Surface structure; nano-structure

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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^+ 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^+ 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, nanostructuration 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^+ 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^+ 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_4 , 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 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 $0.01 - 0.1 \text{ } \Omega\text{cm}$. 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_3 solution for 1 min. Then, the wafers were immersed in the etchant consisting of HF and H_2O_2 solutions. The HF concentration of the etchant was fixed to be 5 M, whereas the H_2O_2 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_3 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_3 solutions. The used

AgNO_3 concentrations, etching times, and resistivity of the substrates are summarized in Table I. Then, silver dendrites on the surfaces were dissolved with HNO_3 solution. The substrates were rinsed and observed by SEM.

Table I Summary of the etching conditions.

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

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 H₂O₂, (b,e) 5-M HF + 0.3-M H₂O₂ and (c,f) 5-M HF + 0.6-M H₂O₂, respectively. In Figs. 2a, the Ag particles are distributed on the whole areas including the ridges as well as the bottoms of the microscaled structures. In Figs. 2b and 2c, 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_3 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_2O_2 concentrations. As the H_2O_2 concentration increases, the pore diameter at the openings becomes larger. In the result of 0.1-M H_2O_2 concentration shown in the black line indicates that the pore size is classified into two groups, nanoscaled and micro scaled pores, as obviously observed in Fig. 2d.

3.2 Chemical wet etching of Ge assisted with electroless-metal-deposition

#1 The AgNO_3 concentration and etching-time dependence

Fig. 4 shows SEM images of the Ge surfaces after the etching assisted with electroless-metal-deposition using AgNO_3 solutions with AgNO_3 concentrations of (a,b,c) 0.01 mM, (d,e,f) 0.025 mM and (g, h, i) 0.05 mM, for (a,d,g) 20 h, (b,e,h) 46 h and (c,f,i) 66 h. Nanostructures and/or microstructures are observed on the Ge substrates, and it is confirmed that size and density of these structures are controlled by the AgNO_3 concentration and the etching time. In Figs. 4a, 4b, 4c, 4d, 4e and 4g, we can observe whisker-like nanostructures on the Ge surfaces, and their length and density depend on the AgNO_3 concentration and the etching time. Fig. 5a shows etching time dependence of the length of the whisker-like structures when the etchant with 0.01-mM AgNO_3 was used. The whisker-like structures become longer, as the etching time is longer. Fig. 5b shows AgNO_3 concentration dependence of the length of the whisker-like structures when the etching time was 20 hours. When the AgNO_3 concentration is higher, whisker-like structures become longer. Fig. 5c shows AgNO_3 dependence of the density of whisker-like structures when the etching time was 20 hours. As the AgNO_3 concentration increases, the density of the whisker-like structure becomes lower. On the

other hand, under the conditions of a long etching time and a high AgNO_3 concentration, the whisker-like nanostructures disappear and microscaled structures like mountains appear, as shown in Figs. 4f, 4h and 4i.

Fig. 6 shows SEM images of Ag particle growth in the etching of Ge assisted with electroless-metal-deposition in the 0.05-mM AgNO_3 solution for (a) 15 h, (b) 28 h and (c) 40 h, where insets are the corresponding Ge surfaces after removal of the Ag particles. The Ag particles grew during the simultaneous metal deposition and became larger as the process time became longer. After 40 h etching, the grown Ag particles coalesced to form a continuous film. As shown in the insets in Fig. 6, the density of the Ge nanostructures decreased and their size became larger for longer etching time, and finally the Ge nanostructures disappeared and microscaled dome-like structures remained on the surface.

#2 The substrates resistivity dependence

We investigated the relation between the substrate resistivity and the morphology after the etching assisted by the electroless-metal-deposition. Fig. 7 shows the SEM images of (a,b) Ag particles grown on the surfaces and (c,d) the corresponding Ge nanostructures, where the Ge substrate resistivity was (a,c) 0.01 - 0.1 Ωcm and (b,d)

0.23 - 0.25 Ωcm . The etching/deposition was performed in the 0.05 mM AgNO_3 solutions for 20 h. Ag particle density on the low-resistivity substrate is higher than that on the high-resistivity substrates, and a more continuous film form on the low-resistivity substrate through Ag particle coalescence compared with the high-resistivity one. In the etching of the low-resistivity substrate, comparatively gentle mountain-like nanostructures are observed, as shown in Fig. 7c, whereas needle-like nanostructures appear in the etching of the high-resistivity substrate, as shown in Fig. 7d. These results indicate that the Ge surface morphology, in particular their sharpness, depends on the substrate resistivity in the present etching.

4. Discussion

4.1 Chemical wet etching of Ge assisted with catalytic-metal-particles

The reactions of Ge in a HF + H₂O₂ solution are expressed as follow.

The whole reaction is expressed as follows [19].

Reaction (1) represents decomposition of hydrogen peroxide by Ag catalyst. The above etching mechanism is similar to that of Si. First, Ge⁴⁺ is generated by the oxidization of Ge under the reactivity of the H₂O₂ solution, and then the Ge⁴⁺ dissolves in the HF solution, resulting in continuous etching of Ge. When the Ge substrates were etched in a HF + H₂O₂ solution without Ag catalyst, no nanostructure forms on the Ge surfaces (experimental results not shown). This indicates that nanostructure formation on the Ge surfaces is accompanied with a reaction assisted with the Ag catalyst. Because the etching rate at the Ag catalyst/substrate interface is higher than that at the etchant/substrate interface, preferential metal-catalyzed chemical etching advances. In the case of Ag-assisted chemical etching of Si in a HF + H₂O₂ solution, the etching

proceeds only at the Ag/Si interface, and the Ag particles penetrate the Si bulk [20]. It was also reported that morphology of the etched surfaces strongly depends on the etchant composition, in particular, the concentration of H_2O_2 [21].

In light of the above mentioned reports as well as our experimental results, we propose a model of metal-assisted chemical etching of Ge, as shown in Fig. 8. Under the condition of a low concentration of H_2O_2 , the Ag particles penetrate the bulk and form many pores vertical to the surface, as shown in Fig. 2a. From this result, we can assign the Ge etching model at low H_2O_2 concentrations to Fig. 8a. When the Ge substrate with Ag catalytic particles is immersed in the etchant, the preferential oxidation reaction occurs dominantly just below the Ag particles through the catalytic function of Ag. Because of low concentration of atomic oxygen (reaction 1), the oxidation rate at the etchant/Ge interfaces is much smaller than that at the Ag/Ge interfaces. The Ge oxide formed in the oxidation process is dissolved by HF into the etchant. When the oxidation/dissolution processes are repeated, the etching at the Ag/Ge interfaces progresses and many vertical holes form. When the H_2O_2 concentration is high, the etching process shifts from Fig. 8a to Fig. 8b, because oxidization reaction of Ge occurs not only at the Ag/Ge interfaces but also at the etchant/Ge interfaces owing to the increased atomic oxygen produced by reaction (1). As a result, the Ge surfaces which

are not covered with Ag were also intensively oxidized by atomic oxygen, then the etching of Ge progresses at both the Ag/Ge interfaces and the etchant/Ge interfaces.

Differences in the etching mechanism between the low and high concentrations of H_2O_2 affect the Ag particle arrangement on the Ge substrates and the morphology on the etched surfaces, as shown in Fig. 8. In a low concentration of H_2O_2 , either the micropore or nanopore forms depending on the density of Ag particles: a high density of Ag particles leads to form the micropores, whereas a low density of the Ag particles forms nanopores. In relatively high H_2O_2 concentrations, independently formed pores merge together and crater-like pores appear.

Next, we compare our experimental results with previously reported studies. C. Chartier et al. [21] conducted Si etching using $\text{HF} + \text{H}_2\text{O}_2$ solutions by changing the solution composition, ρ , defined by

$$\rho = [\text{HF}] / ([\text{HF}] + [\text{H}_2\text{O}_2]) \quad (4)$$

The values of ρ calculated from our experimental conditions are 98%, 94% and 89% for the concentrations of H_2O_2 of 0.1 M, 0.3 M and 0.6 M, respectively. Comparing our etching results with previously reported ones [21], morphology of the Si surfaces etched with $\rho \sim 9\%$ and $\rho \sim 14\%$ are similar to that of the Ge surfaces etched with $\rho \sim 89\%$ and $\rho \sim 94\%$, respectively. Moreover, perpendicular pores with high-aspect ratios that had

been observed on the Si surfaces etched with $\rho > 20\%$ were not observed in our results. Because reactivity of Ge with H_2O_2 is much higher than that of Si, we can conclude that Ge is oxidized much faster than Si. This is one of the reasons why Ge nanowire fabrication by wet chemical etching has been a challenge.

Formation process of Si nanowires in wet chemical etching consists of the following steps: (1) deposition of metallic catalyst particles such as Ag on a Si substrate, (2) preferential oxidation of Si at the interfaces between the catalytic metal particles and the Si substrate surfaces without oxidation in the catalyst-free areas, (3) vertical hole formation through Si etching just below the metal particles without etching on the catalyst-free areas, (4) lateral etching on the sidewalls of the holes and (5) nanowire formation through coalescence of the holes [4,22]. Furthermore, the density and arrangement of the catalyst particles on the substrates also affect the etching morphology. In our experimental results shown in Figs. 2b and 2e or Figs. 2c and 2f, the density of Ag particles were found to be locally too high to form separate, vertical nanoholes in the areas of the crater-like microholes, compared with the previous reports on Si nanowire formation using a wet chemical etching [23]. This suggests that migration control of the Ag particles as well as their initial density plays an important role in nanowire formation. The conditions required to form Ge nanowires using the

metal-assisted wet etching are: (1) penetration of metal particles into the Ge bulk to form vertical holes and (2) an arrangement of the catalytic-metal-particles on the substrate surface that exhibits specific density, size and interval suitable for the hole formation that occurs on Si surfaces. To satisfy these requirements, we have to use an etchant with very low H_2O_2 concentrations or with other oxidation agent whose oxidative power is weaker than H_2O_2 to suppress unfavorable Ge oxidation in the catalyst-free areas. The electroless plating is one of the promising methods because a strong oxidation agent, such as H_2O_2 , is not required to proceed the etching.

4.2 Chemical wet etching of Ge assisted with electroless-metal-deposition

The redox equations in the etching of Ge assisted by the electroless-metal-deposition are expressed as follow, where Ag^+ is an Ag ion in the solution and Ag^0 an Ag atom in the deposited bulk layers.

Total reaction is

Normal electrode potentials of Ag and Ge are

$$E_0 (\text{Ag}^+ / \text{Ag}) = 0.779 \text{ V} \quad (8)$$

$$E_0 (\text{Ge}^{4+} / \text{Ge}) = 0.124 \text{ V} \quad (9)$$

The potential difference is

$$E_0 = 0.779 - 0.124 = 0.655 \text{ V} \quad (10)$$

Many studies on the electroless deposition of noble metal on a Ge substrate have been reported [18,24–28], and it has been revealed that electroless deposition of Ag on Ge surfaces occurs, as shown in Fig. 9. J. Yang et al. [25] reported two possible processes. If electrons in the Ge substrate surface are directly transferred to Ag^+ , Ag islands form

on any area of the surface, resulting in an Ag film that covers the entire surface (process A). If electrons in the Ge substrate are transferred to Ag^+ through the Ag islands formed on the substrate, the Ag islands grow (process B). It was also suggested that process B tend to occur more frequently than process A [25]. Our experimental results suggest that the major process of the Ge etching is process B, but the morphology depends on the AgNO_3 concentration and etching time. Ag nuclei and islands deposited on the Ge surface progressively grow with increase in the etching time and merge to form clusters and, finally, a continuous film. The Ge nanostructures form when the Ag particles penetrate the Ge bulk, and the microstructures form when the Ag particle clusters etch the surface.

From the above discussion, we can conclude that the etching of Ge assisted with the electroless-metal-deposition is subject to the process referred to as process B in Fig. 9. In the early stage, nucleation of Ag particles occurs on the Ge surface through the oxidation-reduction reaction between Ag^+ and Ge (a in Fig. 9, process B). Next, the electrons from the Ge substrate are transferred to the Ag particles via the Ag/Ge interface (b). Then, negatively charged Ag particles selectively gather Ag^+ , and Ag particles grow. The Ge^{4+} produced in this reaction are dissolved in H_2O and removed from the interfaces between the Ge surface and the Ag particles (c). The Ag particles

continuously grow (d) (in this stage, the illustration area is expanded in Fig 9), coalesce and finally become a continuous Ag film (e).

In some reports, Si nanowires can be fabricated using Si etching assisted with electroless deposition of Ag on the Si substrates [29–33]. In these reports, HF + AgNO₃ solutions were used as the etchant. K. Peng et al. [34] showed that deposited Ag particles penetrated the Si bulk vertically without Ag particle growth, and that Ag-particle free areas were left as the Si nanowires when using HF + AgNO₃ solution. In the case of wet etching of Si with HF + AgNO₃ solution, the Si⁴⁺ oxidized with Ag are dissolved in HF solution, whereas in wet etching of Ge with AgNO₃ solution, the Ge⁴⁺ oxidized with Ag are dissolved in H₂O. Therefore, the difference in the solutions to dissolve the oxidants may cause the slow rate of Ge etching, and the etching rate of Si is faster than that of Ge. We conducted Ge wet chemical etching in HF + AgNO₃ solutions, which is representative etchant to form Si nanowires in the etching assisted with the electroless deposition, but the Ge substrate was covered with a consecutive Ag film without nanowire formation (the results not shown). To form Ge nanowires, we should use an etchant that can dissolve Ge⁴⁺ so that Ag particles should penetrate the substrate before forming a continuous film.

5. Conclusion

To fabricate Ge nanostructures on Ge surfaces, we have conducted chemical wet etching of Ge assisted with catalytic-metal-particles and electroless-metal-deposition under various conditions. In the metal assisted chemical etching, we deposited Ag particles on the Ge surfaces using an AgNO_3 solution and etched Ge using $\text{HF} + \text{H}_2\text{O}_2$ solutions. We have succeeded in formation of nanopores on the substrate and found that the pore sidewall inclination angles with respect to the surface can be controlled by H_2O_2 concentrations. These results have revealed the etching processes, but also suggested that Ge nanowire fabrication using the metal-assisted chemical etching would be challenge. In the wet etching assisted with the electroless-metal-deposition, we have successfully fabricated whisker-like nanostructures and indicated that their size and morphology can be varied by changing the AgNO_3 concentration, etching time and substrate resistivity. Furthermore, we have clarified the etching processes assisted with the electroless deposition of Ag on Ge and pointed out the problems to be solved for realization of Ge nanowires using simple wet processes. The findings of this study will lead to a practical production method of Ge nanostructures.

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6. References

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Figures and Captions

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

Fig. 2 SEM images of Ge nanostructures fabricated by etching assisted with catalytic Ag particles in HF + H₂O₂ solutions of (a,d) 5-M HF + 0.1 M-H₂O₂, (b,e) 5 M-HF + 0.3-M H₂O₂ and (c,f) 5-MHF + 0.6-M H₂O₂. (a-c) Before removing the Ag particles and (d-f) after removing them.

Fig. 3 Opening diameter distributions of the pores in the etching assisted with catalytic-metal-particles. Black line is for H_2O_2 concentration of 0.1 M, red one 0.3 M and green one 0.6 M.

Fig. 4 #1 SEM images of the Ge nanostructures after the etching assisted with electroless-Ag-deposition using AgNO_3 solutions with concentrations of (a,b,c) 0.01 mM, (d,e,f) 0.025 mM and (g, h, i) 0.05 mM, for (a,d,g) 20 h, (b,e,h) 46 h and (c,f,i) 66 h.

Fig. 5 (a) Mean length of whisker-like nanostructures fabricated by the Ge etching assisted with electroless-Ag-deposition (a) after the etching in a 0.01-mM AgNO_3 solution as a function of etching time and (b) after the 20 h etching as a function of AgNO_3 concentration. Each error bar indicates a standard deviation. (c) Density of the nanostructures after the 20 h etching as a function of the AgNO_3 concentration.

Fig. 6 SEM images of Ag particle size and distribution after the Ge etching assisted with electroless-Ag-deposition in a 0.05-mM AgNO_3 solution for (a) 15 h, (b) 28 h and (c) 40 h. Insets are Ge surfaces after removal of the Ag particles.

Fig. 7 SEM images of the Ge surfaces formed by the etching assisted with electroless-Ag-deposition in the 0.05-mM AgNO_3 solution for 20 h: (a,b) Ag particles grown on the surfaces and (c,d) the corresponding Ge nanostructures. The resistivity of the Ge substrates was (a,c) $0.01 - 0.1 \Omega \text{cm}$ and (b,d) $0.23 - 0.25 \Omega \text{cm}$.

Fig. 8 Schematic illustration of the etching processes assisted with catalytic-metal-particles in a 5-M HF and H_2O_2 etchant: (a) relatively low H_2O_2 concentration and (b) relatively high H_2O_2 concentration.

Fig. 9 Schematic illustration of the Ge etching assisted with electroless-Ag-deposition: process A is for electron transfer via the etchant/Ge interfaces and process B for electron transfer via interfaces between the Ag particles and the Ge surface.