Fabrication of Si-nanowires controlled by spontaneously formed nanoholes on annealed
Au thin films

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Abstract

Si nanowires (Si-NWs) were fabricated by a simple process that consists of deposition of Au thin films, annealing of the Au films to form porous structure and Si wet-etching using the kinetically appearing porous Au films as a template. The deformation behavior of the Au thin films was investigated by scanning electron microscopy and atomic force microscopy. The nanohole diameter and density of the Au films can be controlled by selecting Au film thickness, annealing temperature and annealing time. The formation mechanism of these porous Au films can be explained by a model that consists of nanohole formation at the grain boundaries of the Au films and ridge formation by Au atom diffusion to the hole periphery. The ridge structure suppresses further deformation

of the Au films and keeps the nanohole structure kinetically stable. When a thermal energy larger than the activation energy to destroy the ridge structure is supplied, it transforms to the island structure.

Keyword

Si nanowire, porous Au film, wet etching

1. Introduction

Si nanowires (Si-NWs) are one of the most promising candidates for materials in the advanced future electronic, photonic and energy devices, such as field effect transistors [1][2][3][4], solar cells [5][6][7][8] and lithium ion batteries (LIBs) [9][10][11][12][13]. To apply Si-NWs to these devices, techniques to control their diameter and density are necessary. One of the Si-NW fabrication methods is the vapor-liquid-solid (VLS) growth [12][14][15]. However, dangerous gasses, such as silane and phosphine, are used in the VLS method. To fabricate Si-NWs, we used the metal-assisted chemical etching (Mac etching) [16][17][18] catalyzed by a noble metal whose schematic process is shown in Fig.1. In this technique, size and density of the fabricated NWs are determined by the catalyst metal morphology, and Si nanostructures can be fabricated easily, safely and at low cost. Moreover, electroless metal deposition (EMD) method [19][20] using AgNO_3 and HF mixed solution can be applied to catalyst formation in the Mac etching.

To control diameter and density of Si-NWs, application of porous anodic alumina (PAA) [21][22] to a template of the wet etching was reported [23][24], as illustrated in Fig.1. PAA fabricated by anodic oxidation of aluminum in an electrolyte is a nano-scaled porous structure whose diameter and density are controllable. Generally, Si-NWs fabricated by the Mac etching assisted by the EMD method are non-uniform and thick (about 30-250

nm [19][20]). In the PAA template method, ultra-thin NWs (-10 nm [24]) with a uniform diameter can be fabricated. But, this technique consists of many steps including PAA template fabrication, metal deposition and Si etching.

In this study, we used nanoporous Au thin films that self-assemble as a metastable state on a Si substrate only through thermal annealing to fabricate Si-NWs without conventional lithography or self-assembled masks, such as the PAA templates. We show structural evolution of the porous Au films during the annealing and discuss its mechanism.

2. Experimental procedures

Si-NWs were prepared by the Mac etching of n-Si (100) substrates with the resistivity of about 1-2 Ωcm . The substrates were organically cleaned in acetone, ethanol and deionized water for 5 min each in an ultrasonic bath. After the cleaning, 5, 15 or 30 nm thick Au thin films were deposited by vacuum evaporation from Au wire (99.99 %) under pressure lower than 7.8×10^{-4} Pa.

Au evaporation was carried out by resistive heating of a tungsten basket containing the Au wire as source material. The film thickness can be calculated according to the following equation by assuming that the source material was isotropically evaporated,

spherically spread and uniformly deposited.

$$T = V / 4\pi L^2$$

where T is film thickness, V volume of evaporation material and L distance between the substrate and the source material. Au was chosen as catalyst material from noble metals, Au, Ag and Pt. We found that agglomeration control of Ag films is difficult because their porous structures are not stable and quickly transformed to island structures without the subsequently described metastable state. Nanoporous Pt films are also difficult to obtain using an ordinary furnace because the melting point of Pt is 1768 °C.

After Au deposition, the samples were annealed in air at temperatures from 100 to 500 °C to form porous Au films. All samples were taken out from the oven and cooled to room temperature. The samples were observed by atomic force microscopy (AFM). Then, the Au/Si samples were immersed in the etching solution that contained 5 M HF and 0.5 M H₂O₂ for 30 min to fabricate Si-NWs. After the etching, the samples were rinsed in deionized water and dried in an oven at 120 °C.

Influence of the chemical states of the substrate surface on the Au film deformation during annealing was investigated using Si substrates treated before the Au deposition using different solutions: a mixed solution of H₂SO₄ and H₂O₂ with a volume ratio of 3:1 (piranha solution), where the substrate surface is covered with a Si-oxide layer terminated

with hydroxyl groups [25], and a HF solution, where the surface is oxide-free and terminated with atomic hydrogen.

We also fabricated Si-NWs using the PAA membrane as a template to compare morphology of the Si-NWs fabricated by different templates. Al films of 100 nm were deposited on HF-treated Si substrates by the vacuum evaporation, and anodic oxidation was performed in 0.3 M oxalic acid at 80 V to fabricate the PAA template. After that, the samples were immersed in 3 wt% phosphoric acid for 30 min to expand the pores. Au films of 15 nm thickness were deposited by the vacuum evaporation to form an Au mesh on the PAA top surface and Au particles on the bottom surfaces of the PAA holes. The Au particles would not influence the etching process because the Si etching rate at the Au nanoparticles/Si interfaces is much slower than that at the Au mesh/Si interfaces [24]. Si-NW fabrication procedure was the same as that for the porous Au template method. In the early stage of the etching, the PAA template between the Si substrate and the Au mesh is removed by the HF solution. After that, the Au mesh was precipitated on the Si substrate, and the Si surface was preferentially etched at the Au-mesh/Si interface [23].

In the whole experiments, Si substrate surfaces were observed by scanning electron microscopy (SEM).

3. Results and discussion

Figure 2 shows morphology of the 15-nm Au thin films (a) before annealing, after annealing at (b) 200 °C, (c) 300 °C and (d) 400 °C for 3 min. The hole sizes are small and elongated (typically 100×10 nm) upon the 200 °C annealing, as shown in Fig. 2(b), and becomes larger as the annealing temperature increases, as shown in Fig. 2(c)-(d). Therefore, it can be confirmed that the hole size is controllable based on the annealing temperature. M. A. George et al. reported [26] that micro-sized (about 3-5 μm) porous Au structure could be formed from 85-nm Au films that were deposited by electron beam evaporation and annealed at 600-650 °C for 60 min. In this case, agglomeration was observed when annealed at 700 °C for 60 min. These morphological changes are thermally induced because the Au/SiO₂ adhesion force is not strong.

Figure 3 shows SEM images of (a) (b) 5-nm and (c) (d) 15-nm Au thin films. Figures 3 (a) and (c) show as-deposited surface and (b) and (d) annealed ones at 200 °C for 3 min. From these figures, we can confirm that hole density becomes larger as original Au film thickness decreases. The hole density in Fig. 2(b) is $120 \mu\text{m}^{-2}$ and that in Fig. 3(b) $250 \mu\text{m}^{-2}$. Figure 2 (b) and Fig. 3 (b) were taken for different Au film thickness, 15 nm and 5 nm, respectively, under the same annealing conditions, at 200 °C for 3 min. Therefore, the hole density is controllable by the Au film thickness. The hole shape is near-ellipse in

the 5-nm Au films. For application of Si-NWs to anode materials of LIBs, nanowires with the ellipsoidal cross-sectional shape is often more favorable for fast Li ion absorption than the circular cross section during the charge/discharge cycles because of their larger surface areas.

Figure 4 shows annealing time dependence of morphology of the 15-nm Au films at (a) (b) 200 °C for 10 and 30 min, and (c) (d) 500 °C for 3 and 10 min. In Fig. 4 (d), the Au film was agglomerated to form an island structure. On the other hand, in Fig. 4 (a) and (b), agglomeration of the Au thin films accompanied with island formation was not observed. This means that porous structure can be kept basically unchanged for low temperature annealing.

Based on the above-described results, we suggest that nano-porous structure is kinetically metastable structure before transition to the island structure, and we propose a model that explains the observed morphological change, as shown in Fig. 5, where h is an as-deposited Au film thickness, h' height of a ridge that formed during the annealing, r width of the ridge, D distance between the ridges and R diameter of a hole. In this model, we hypothesize that the hole shape is circular in stage 2. Figure 5 (a) shows a cross-sectional view of as-deposited films and substrate in stage 1, which corresponds to Fig. 2 (a), where many voids form from the initial grain boundaries.

When large thermal energy is supplied by annealing, surface diffusion of Au atoms occurs. This atom transport partially uncovers the surface to reduce surface free energy [27][28][29][30]. The voids are expanded by this mechanism and transition from stage 1 to stage 2 occurs. Some different mechanism have been proposed for void nucleation site in the literature [30]. However, in the present study, it is obvious that voids in the as-deposited films are expanded by the annealing, as confirmed by the elongated pores in the annealed films. The onset temperature of film deformation increased with increase in the film thickness. When the temperature does not reach the onset temperature, the films maintain their original morphology. This result agrees with the previous report [29].

In stage 2, the Au atoms located at the edge of the voids were transported to the Au film inside, which causes void expansion and film edge growth, as shown in Fig. 6, where a 30 nm Au film was annealed at 400 °C for 30 min. In this stage, the porous structure formation is attributable to the metastable contact angle at the ridge of the nanoporous Au films, which suppresses transition to the island structure.

As previously mentioned, Au thin film agglomeration caused by annealing transforms the Au films to the island structure to decrease the surface free energy. Generally, stability of the metal/substrate/atmosphere system is increased as the area of metal/substrate

interface is decreased. But, when focusing on the local stability of the individual ridge areas, the contact angle of the metal is determined by the following Young equation:

$$\cos \theta = \frac{\gamma_{SiO_2} - \gamma_i}{\gamma_m}$$

where γ_i , γ_{SiO_2} and γ_m are interface energies between metal and the substrate, atmosphere and the substrate, and atmosphere and metal, respectively (see Fig. 7). When the local contact angle exceeds an angle determined by this formula, the metal agglomeration stops without the transition to the island structure. It is difficult to directly measure the contact angle of nanoscale metal particles, but the mound height should become higher as contact angle increases. We can qualitatively discuss the metastable porous structure using the mound height instead of the contact angle.

Figure 8 shows temperature dependence of the ridge height. In stage 2, growth of the ridge stops when h' reaches a saturated height that is determined by the annealing temperature shown in Fig. 8. D becomes smaller when the deformation is in progress, but if h' reaches the saturated height before D reaches 0, in other words, as long as a ridge does not reach another side, the Au-uncovered holes are preserved, and the Au island structure will not form even if annealing time is extended. Additionally, in this case, r becomes larger, if the original thickness, h , is large. When the annealing temperature is sufficiently high, the deformation of the Au film progresses and transition from stage 2

to stage 3 occurs, as demonstrated in Fig. 9.

In stage 3, as a result of the agglomeration progress, island structure is formed by coalescence of the holes that isolates the Au films areas. Although the island height becomes larger with increase in the annealing temperature, the density is independent of the temperature. J. Y. Kwon et al. also reported [30] that island diameter and density are independent of the temperature in Au/SiO₂ system.

Figure 9 shows morphology of ridges during the transition from stage 2 to stage 3 on a sample with 30-nm Au thin film annealed at 500 °C for 30 min. In Fig. 9 (a), ridges forming islands (for example, A) and those still existing at the periphery of the Au film area (for example, B) coexist. Figure 9 (b) shows cross-sectional view along the straight line in panel (a). The island-like ridge is higher than that at the Au film periphery. This height difference is probably caused because the island-like ridge can collect more Au atoms owing to isolated location. For example, island-like ridges can collect atoms from the both sides, while ridges at the Au film periphery can collect atoms from only one-side. In Fig. 9 (a), coalescence of holes that separates ridges is also demonstrated (for example, C and D).

Figure 10 shows morphology of 15-nm Au thin films deposited on (a) the organically cleaned, (b) the piranha-treated and (c) the HF-treated surfaces and annealed at 200 °C

for 30 min. Porous structures are observed in Figs. 10(a) and 10(b), and Au agglomeration and transition to the island structure occur in Fig. 10(c). By comparing Fig. 10(a) with 10(b), it is suggested that the adhesion force between Au films and the piranha-treated surface is smaller than that on the organically treated surface. Because hole area in Fig. 10(c) is larger than that in Fig. 10(b), adhesion force between the Au films and the oxide free Si surface is much smaller than the other interfaces. Therefore, Au film deformation during the annealing is affected by the substrate surface state that determines adhesion force between the substrate and the Au films. We suggest that surface states before Au deposition is also one of the important factors for Au nanopore formation suitable for the Si-NW fabrication. We indicated that conventional organic cleaning can also be used as a surface treatment method before Au deposition to control diameter and density of Si-NWs.

We fabricated Si-NWs using PAA templates as reference samples. Porous Au films with various hole sizes were fabricated by annealing Au films on the PAA templates on Si substrates, as shown in Fig. 11, where a 15-nm Au film was deposited on a PAA template and annealed at 200 °C for 30 min. The Au mesh fabricated on the PAA template was little deformed by the annealing.

Figure 12 shows Si-NWs fabricated using (a-f) the spontaneously formed porous Au

We further discuss the size and density controllability in the porous Au film method based on Table I and Fig. 12. All porous Au films, regardless of pore size, can be used to fabricate Si-NWs. Because size and density of Si-NWs are determined by the hole patterns of the Au films (see Fig.1), they can be controlled by Au film thickness, annealing temperature and annealing time, as demonstrated in Figs. 2 and 3. For example, density of the SiNWs in Figs. 12(a) and 10(d) is larger than that in Figs. 12(e) and 10(f), indicating that it is controllable by selecting the Au thickness. From comparison between the Si-NWs fabricated using the PAA templates (Figs. 12(g) and 12(h)) and those using the Au thin films (Fig. 12(e) and 12(f)), the PAA template process can be replaced by the simple annealing of the Au thin films. Although fabrication of uniform Si-NWs is difficult by this technique, their local non-uniformity is not a serious problem in the application to LIBs because LIB anodes are much larger than the Si-NWs and the local non-uniformity is leveled.

Therefore, the present process is promising for fabrication of the Si-NWs whose diameter and density are controllable.

4. Conclusion

We have found that nano-scaled porous structures can be fabricated on Au thin films by

a simple process where their size and density are controllable by selecting appropriate film thickness, annealing temperature and annealing time. The observed spontaneous formation of porous Au films can be interpreted by a model that consists of nanopore formation at the grain boundaries of the Au films, ridge formation by Au atom diffusion to the hole periphery and its local metastability that suppresses further deformation of the Au films. If agglomeration of Au films exceeds a critical level, transition from porous structure to islanding one occurs. In conclusion, Si-NWs can be fabricated by a simple method that consists of deposition of Au thin films on Si substrate, annealing and wet etching.

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Figures

Fig. 1 Schematic illustration of Si nanowire fabrication method

Fig. 2 SEM images of the 15-nm Au films annealed at several temperatures: (a) before annealing, and after annealing at (b) 200 °C, (c) 300 °C and (d) 400 °C. The inset in panel (d) is a wide view.

Fig. 3 SEM images of the 5 and 15-nm Au films annealed at 200 °C for 3 min.:

(a) 5-nm and (c) 15-nm Au films before annealing, and (b) 5-nm and (d) 15-nm Au films after annealing at 200 °C for 3 min.

Fig. 4 SEM images of the 15-nm Au film annealed at several temperatures and times:

(a) annealing at 200 °C for 10 min and (b) 30 min, and (c) annealing at 500 °C for 3 min and (d) 10 min. The insets in panels (c) and (d) are wide views.

Fig. 5 Phenomenological model describing fabrication of the island structure through the hole structure.

Fig. 6 AFM image of 30-nm Au film annealed at 400 °C for 30 min.

Fig. 7 Contact angle at the ridge of the nanoporous Au films.

Fig. 8 Annealing temperature dependence of the ridge heights.

Fig. 9 Transition from stage 2 to stage 3 and comparison of a ridge and an island heights.

Fig. 10 SEM images of the 15-nm Au films deformed by annealing at 200 °C for 30 min. The original surfaces before Au film deposition were treated with: (a) organic solvents, (b) piranha solution and (c) HF solution.

Fig. 11 SEM image of an annealed Au film on the PAA template.

Fig. 12 SEM images of the Si-NWs fabricated using (a-f) the spontaneously formed porous Au film method, and (g,h) the PAA template method. Details of the fabrication conditions are listed in Table I.

Table I. Conditions of Au the template preparation for Si-NWs displayed in Fig. 12.

Si-NWs	template *	Au thickness [nm]	Temperature [°C]	Annealing time [min]	Corresponding SEM image of the template
Fig. 12a,b	PAF	5	200	3	Fig. 3b
Fig. 12c,d	PAF	15	200	3	Fig. 2b
Fig. 12e,f	PAF	15	400	3	Fig. 2d
Fig. 12g,h	PAA	15	200	30	Fig. 11

(* PAF: Porous Au film, PAA: Porous anodic alumina)