Au-Ge eutectic droplet formation on the initial stage of selective-area VLS growth of Ge nanowires on Si (111)

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1. Introduction

Semiconductor nanowires (NWs) have recently attracted great attention as a building block candidate to overcome the physical limitations associated with device miniaturization and high degree of integration [1]. Our long-term research aim is to realize a promising device architecture called the vertical gate-all-around (GAA) NW transistors, which utilize semiconducting Ge NWs to break through the device performance.

The vapor–liquid–solid (VLS) method is one of the most widely-used techniques for Ge NW synthesis, utilizing phase transitions of materials. In this method, when a precursor gas is supplied to a solid metal catalyst (typically gold), the metal absorbs the gaseous precursor, and then, forms a eutectic liquid droplet. Continued gas supply leads to supersaturation within the droplets, eventually causing the Ge atoms to precipitate at the interface between the droplets and the substrate, resulting in the epitaxial growth of NWs. The eutectic droplets composed of catalyst metal and precursor atoms are formed at a temperature significantly lower than the melting point of pure catalysts (e.g., 361°C in the case of Au–Ge) [2].

Our goal for the GAA-NW transistors is to establish a technique that enables vertical Ge NW growth with precisely controlled position and diameter by using electron beam (EB) lithography and conventional lift-off processes to define the location and size of circular Au thin film patterns. However, as the vertical Ge NW growth via the VLS method above remains still challenging, understanding the behavior of Au–Ge eutectic droplets during the initial stages of growth is crucial. In this paper, therefore, we characterize the behavior of Au catalysts (i.e., Au–Ge eutectic) on the initial stages of selective-area VLS growth of Ge NWs heterogeneously on Si (111) substrates.

2. Experimental Procedures

Figure 1 shows a schematic diagram of the selective-area VLS growth process for Ge NWs. An EB resist was applied to a Si (111) substrate with the native oxide film removed, and a periodic aperture pattern was fabricated by EB lithography. The 30-sec immersion in BHF (HF: NH_4F = 1: 10) was used to remove the native oxide film, and 8-nm-thick Au thin films were deposited. The Au thin films were then periodically placed by the lift-off process. Before the growth, native oxide films were again removed by HF treatment, and the substrates were annealed at 360°C. The VLS growth of Ge NWs was performed during the GeH_4 gas supply at a partial pressure of 58 Pa (4, 7, 10, and 20 min) and a growth temperature of 360 °C. The carrier gas during the VLS growth was N_2. Scanning electron microscopy (SEM) was used to characterize the Au–Ge eutectic droplet formation and the Ge NW growth at the initial stages of VLS.

3. Results and Discussion

Figure 2 shows the average diameters (D) of circular Au thin film catalyst patterns for Ge gas supply times of 0, 4, 7, 10, and 20 min, with the corresponding top-view SEM images at each of the Ge gas supply times. The D initially at 0 min measured approximately 157 nm, and then, it increased a bit to around 195 nm at 4 min. However, comparing the D of Au patterns, the D abruptly decreased to 74 nm at 7 min, and, finally, no further significant changes were observed at 10 and 20 min. The bird's-eye view SEM image (the image in the green box) at 10 min markedly shows that each of the catalyst patterns has taken mostly a spherical shape. As there is little variation in diameter, judging from the SEM image contrasts, after the gas supply time of 7 min, it is reasonable to infer that the patterns had become spherical by the annealing time of 7 min. The catalyst volume at 7 min, approximated as a sphere, was calculated to be 2.1×10^5 nm³ (D = 74 nm at 7 min). In comparison, the initial catalyst volume, assumed to be a cylinder with a height of 8 nm (D = 157 nm at 0 min), was 1.5×10^5 nm³. The difference in volume corresponds to approximately 29% of the total volume after 7-min annealing. Given that the Au–Ge eutectic system forms a eutectic droplet at 361 °C with a Ge content of 28% [2,3], this volume increase provides strong evidence that the catalyst was in a liquid state and had agglomerated by the annealing time of 7 min.

Figures 3(a) and 3(b) subsequently show the observation results in the back-scattered electron (BSE) imaging mode for the cases of 0 and 7 min, respectively. (The acceleration voltage was set to 3.0 kV.) In the BSE images, the elements with higher atomic number (*Z)* appear brighter, while those with lower *Z* appear darker [4]. At the Ge gas supply time of 0 min, the circular catalyst patterns should remain as a pure Au thin film, and the image in Figure 3(a) with no contrast inside is thus consistent with the observations in Figure 2. In contrast, Figure 3(b) shows a slightly darker contrast near the center of each of the circular Au patterns. At 7 min, the catalyst patterns are assumed to be in a eutectic state composed of Au and Ge. Given that Ge (Z = 32) has a lower atomic number than Au (Z = 79), the regions with higher Ge content should appear darker. Therefore, the observed contrast in Figure 3(b) suggests that the Ge concentration in Au–Ge eutectic droplets may possibly be higher at the center.

Comparing the SEM images at 10 min and 20 min in Figure 2, as there is no significant difference in the length of NWs, we conclude that the GeH_4 partial pressure of 58 Pa may not be sufficient for the growth rate of Ge NWs. Additional experiments thus were conducted to increase the GeH_4 partial pressure after the catalyst aggregation, as shown in the SEM images in Figure 4. In Figure 4(a), following the 7-min annealing at 58 Pa, an additional 5-min annealing at 230 Pa was carried out at the same temperature of 360 °C. A bit longer NWs were obtained, comparing to those in the 20-min sample in Figure 2. In Figure 4(b), when the growth temperature was lowered to 330 °C during the increase in GeH_4 partial pressure, longer NWs with kinks were formed although the uniformity of NWs became poor.

4. Conclusions

In this study, we investigated the behavior of the Au–Ge eutectic at the initial stages of Ge growth toward the vertical growth of Ge NWs via the VLS method. When Ge gas was supplied to Au thin film patterns, we observed that the circular Au disk patterns transformed into an Au–Ge eutectic liquid and, subsequently, aggregated into a spherical form at a certain point (between 4 and 7 min) of the annealing at 360 °C. In addition, we confirmed that a higher GeH_4 partial pressure and a lower growth temperature led to the faster Ge NW growth. However, the growth at the low temperature of 330 °C tended to have a poor uniformity, implying a trade-off between the growth rate and the structural uniformity of Ge NWs.

References

[1] H. T. Ng *et al*., Nano Lett. **4**, 1247–1252 (2004)
[2] S. Kodambaka *et al*., Science **316**, 5825 (2007)
[3] N. Wang *et al.,* Mater. Sci. Eng. R **60**, 1 (2008)
[4] G. E. Lloyd, Mineralogical Magazine **51**, 3-19 (1986)

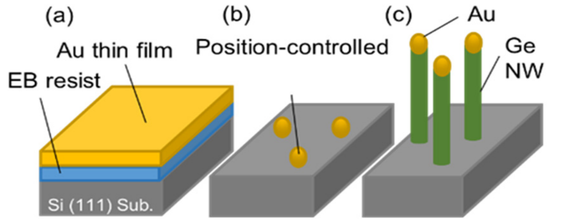

Fig.1 Schematic illustrations of the selective-area VLS growth process for Ge nanowires (NWs).

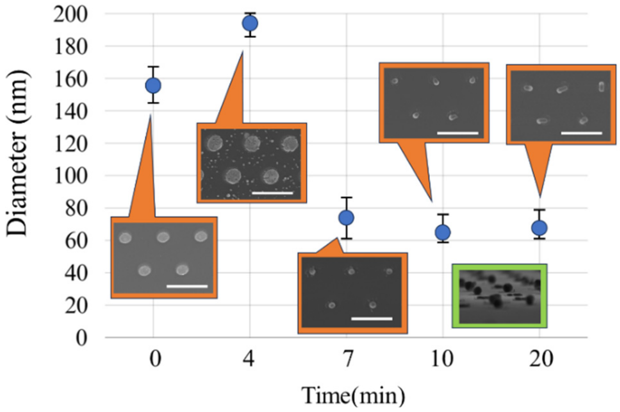

Fig. 2 Change in diameter of the Au thin film catalyst patterns with the corresponding top-view SEM images in the orange speech bubbles at each of the annealing times. White scale bars in the top views represent 500 nm. The SEM image outlined in the green box is a bird's-eye view for the 10-min sample.

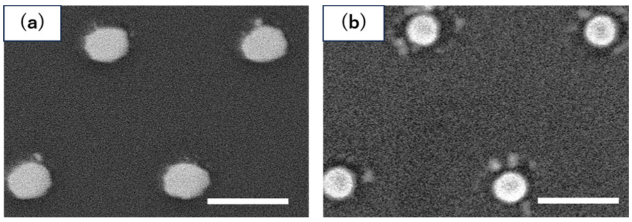

Fig.3 BSE images for the samples with the annealing times of (a) 0 min and (b) 7 min. White scale bars represent 250 nm.

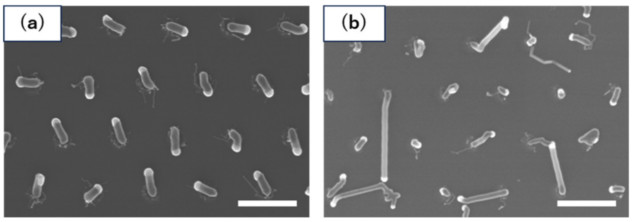

Fig.4 SEM images for the samples in which GeH_4 was supplied for an additional 5 min at 230 Pa after the initial 7-min annealing in Figure 2 at 58 Pa. The temperature during the additional GeH_4 supply at 230 Pa was (a) 360 and (b) 330 °C, respectively. White scale bars represent 500 nm.