Au-Ge eutectic droplet formation and analyses for selective-area VLS growth of Ge nanowires on Si (111)

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1. INTRODUCTION

Semiconductor nanowires (NWs) are attracting significant attention as a possible structural solution to overcome physical scaling limits of semiconductor device miniaturization and high degree of integration. Therefore, extensive research on their growth and application has been conducted in recent years [1]. Germanium (Ge) possesses, in particular, higher electron and hole mobilities than silicon (Si) and favorable physical properties for integration with spintronic devices [2, 3]. Our research aims at realizing vertically aligned, self-standing spin transistors utilizing Ge NWs. The vapor–liquid–solid (VLS) method is one of the most widely adopted techniques for the synthesis of Ge NWs and requires a catalyst metal to nucleate eutectic droplets for starting the NW growth. This process exploits phase transitions of the catalyst material. Upon supplying a precursor gas to the catalyst metal (Au in this study), a liquid eutectic phase is formed at a temperature significantly lower than the melting point of pure Au, i.e., approximately 360 °C for the Au–Ge system [4]. Continued gas supply leads to supersaturation of the precursor element within the catalyst metal, initiating the epitaxial NW growth at the interface with the substrate. In our study, we employ electron beam (EB) lithography and lift-off techniques to precisely position Au thin film patterns, aiming to establish site-selective (or selective-area), vertically aligned Ge NW growth via the VLS method using Au catalysts. In this paper, we characterize the behavior of Au catalysts, i.e., Au–Ge eutectic droplets, 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 site-selective growth process. An EB resist was applied to a Si (111) substrate after a native oxide film was removed from the Si surface, and a periodic aperture pattern was fabricated by EB lithography. The 30-sec-immersion in BHF ($HF:NH_4F$ = 1:10) was conducted to remove a native oxide film. Next, 8-nm-thick Au thin films were deposited. They were then periodically placed by lift-off. Before the VLS growth, native oxide films were removed again by HF treatment and annealed at the temperature of 360°C. The VLS growth of Ge NWs was performed with GeH_4 source gas at a partial pressure of 58 Pa and a growth temperature of 360°C for 4, 7, 10, and 20 min. The carrier gas during the chemical vapor deposition was N_2. Scanning electron microscopy (SEM) was used to evaluate the NW growth.

3. Results and Discussion

Figure 2 shows the average diameters (D) of circular Au catalyst patterns at Ge gas supply times of 0, 4, 7, 10, and 20 min, with the corresponding top-view SEM images at each of the 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. Attention is subsequently directed to the SEM images. The bird's-eye view SEM image (the image on the right side) at 10 min markedly shows that each of the catalyst patterns has taken mostly a spherical shape. As there is little variation in diameter (or SEM image contrast) after the gas supply time of 7 min, it is reasonable to infer that the patterns had become spherical by 7 min. Given that the initially deposited Au film is assumed to be a thin cylindrical shape with a height of 8 nm, the change in both diameter data and SEM morphology suggests that the Au–Ge alloy became a fully-molten eutectic liquid and reconfigured into spherical droplets between 4 and 7 min of Ge gas supply. This interpretation can be further supported by considering volume changes. The volume of the initial circular Au thin film patterns at 0 min, approximated as a cylinder with D = 157 nm and the height = 8 nm, is estimated to be 1.5×10^5 nm³, whereas the volume of droplets at 7 min, assuming a spherical shape with D = 74 nm, is estimated to be about 2.1×10^5 nm³. This suggests that an increase in volume is likely due to the incorporation of Ge atoms during the formation of Au–Ge eutectic droplets. The difference in volume corresponds to approximately 29% of the total volume after 7 min. Given that the Au–Ge eutectic system forms a eutectic droplet at 360 °C with a Ge content of 28% [4,5], this volume increase provides strong evidence that the catalyst was in a liquid state, and had agglomerated by the gas supply time of 7 min.

Figures 3(a) and (b) subsequently show the observation results in the back-scattered electron (BSE) imaging mode for the cases of 0 and 7 min, respectively. The BSE imaging enables us to detect image contrast based on the atomic number (Z) of materials in the samples. Elements with higher Z appear brighter, while those with lower Z appear darker in the BSE images [6]. In this study, the acceleration voltage of incident EB was set to 3.0 kV. At this energy of EB, the estimated maximum penetration depth of electrons is approximately 41.0 nm for the pure Au and 54.5 nm for the Au–Ge eutectic alloy (here, Au:Ge =72:28) [7]. Figure 3(a) shows that no discernible image contrast was observed among the circular Au patterns. At the gas supply time of 0 min, the catalyst remains as a pure Au thin film, and the image with no contrast inside is thus consistent with the understanding in Figure 2. In contrast, Figure 3(b) reveals 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 are expected to appear darker. Therefore, the observed contrast suggests that the Ge concentration in the Au–Ge eutectic droplets may possibly be higher at the center. Figure 4 schematically summarizes the possible formation process of Au–Ge eutectic droplets and Ge NWs under the current experimental conditions; Au film thickness of 8 nm, GeH_4 partial pressure of 58 Pa, and annealing temperature of 360 °C. After no annealing state in Figure 4(a), the Au thin film starts to incorporate Ge, and gradually forms eutectic regions from the Au surface at around 4 min in Figure 4(b). In Figure 4(c), between 4 and 7 min, the entire catalyst transforms into a spherical eutectic droplet. A Ge concentration gradient may form in the droplet, with Ge enriched to the center. In Figure 4(d), finally, continued annealing and gas supply lead to supersaturation at the droplet–substrate interface, initiating the NW growth from the interface.

4. Conclusions

In this study, we investigated the behavior of the Au–Ge eutectic patterns during the initial stages of Ge growth in order to achieve the site-selective vertical growth of Ge NWs via the VLS method. When GeH_4 was supplied to the circular Au thin film patterns, we observed that the Au patterns absorbed Ge while maintaining their shape by 4 min. At the gas supply time of 7 min, the entire catalyst transformed into an Au–Ge eutectic liquid, and then, subsequently aggregated into a hemispherical form. The BSE analyses also showed that the Ge concentration was possibly high at the center of Au-Ge droplets.

References

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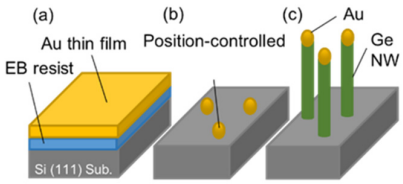

Fig. 1 Schematic illustrations of the selective-area VLS growth process for Ge nanowires (NWs).

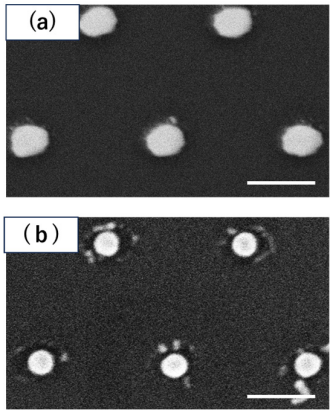

Fig. 3 BSE images of (a) 0 min and (b) 7min. White scale bars represent 250 nm.

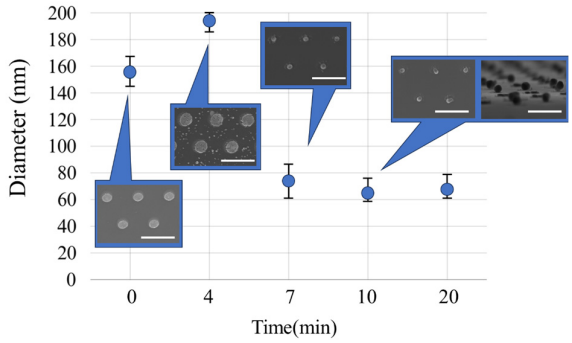

Fig. 2 Change in diameter of the Au thin film catalyst patterns with the corresponding top-view SEM images at each of the annealing times. White scale bars in the top views represent 500 nm while the one in the bird's-eye view at 10 min represents 250 nm.

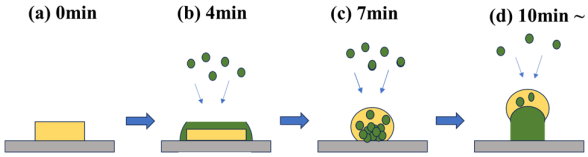

Fig. 4 Schematic illustrations for possible aggregation process of Au thin film catalyst patterns (yellow) with Ge (green).