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Growth of Ultrathin Ge Crystal Layer by Surface Segregation and Flattening of Ag/Ge Structure

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Abstract We have successfully formed ultrathin Ge crystal layers on atomically-flat Ag surface by the annealing of Ag/Ge(100) and Ag/Ge(111) in N_2 ambience. In this work, surface flatness and crystallinity of segregated Ge layer induced by the annealing of Ag/Ge structure were systematically investigated to get an insight into the growth kinetics of two-dimensional (2D) Ge crystals.

1. Introduction

2D crystals of honeycomb lattice with Si and Ge elements such as silicene and germanene are currently receiving much attention because of its exceptional electronic properties [1, 2]. In our previous work, we have demonstrated the formation of not only ultrathin Ge crystal but also 2D crystal on hetero-epitaxial Ag/Ge(111) using Ge surface segregation by annealing [3-5]. From this fabrication technique, surface flattening is quite important as well as the Ge segregation. In addition, one of the key issues for the characterization of its electronic structure and the fabrication of devices is to improve the chemical and thermal stabilities of Ge 2D crystals. Therefore, impact of Ge substrate orientation on the growth of ultrathin Ge crystal and the stability of surface morphology have been investigated in this work.

2. Experimental Procedure

After the cleaning of p-type Ge(111) and Ge(100) wafers by 4.5% diluted HF solution and vacuum annealing at 400 ºC at ~4×10^{-6} Torr, Ag layer in the thickness of ~100 nm was deposited by thermal evaporation using Ag target at base pressure of 4×10^{-7} Torr. From EBSD and XRD analyses, hetero-epitaxial growth of Ag layer on Ge substrate was confirmed. Then, the samples were dipped in by 4.5% diluted HF solution, and subsequent annealing was performed in N_2 ambience at the atmospheric pressure to enhance the Ge segregation and surface flattening.

3. Results & Discussion

Change in the surface morphology for the hetero-epitaxial Ag/Ge(100) structure by the annealing was systematically investigated by AFM in the tapping mode as shown in Fig. 1. AFM image of the samples before annealing shows a rough surface with a root-mean-square (RMS) roughness of 1.0 nm. After the annealing at 300 ºC, a very flat surface with an RMS roughness of 0.6 nm was obtained. Moreover, the unique quadrangular structures, which mainly originate from the crystallographic structure at the surface, was clearly observed in a parallel to the cleavage plane of Ge(100) substrate. With further increase in the annealing temperature, surface roughening occurred. These results indicate that the surface migration of Ag atoms proceeds by the annealing below eutectic temperature of Ag-Ge system (651 °C) [6]. A similar result was also observed for the hetero-epitaxial Ag/Ge(111) as shown in Fig. 2. Initial surface roughness of was slightly larger by ~0.3 nm than that for the sample with Ge(100). Obviously, a very flat surface with threefold rotational symmetry structure was detected after the annealing at 450 °C, which temperature was higher than that of case with Ge(100) by ~150 ºC. These unique surface morphologies indicates that the orientation of ultrathin Ge crystal layer is controlled by the surface orientation of the Ge substrate.

Measured RMS roughness for the hetero-epitaxial Ag on Ge(100) and Ge(111) from AFM images was plotted as a function of the annealing temperature (Fig. 3). For the sample with Ge(100), surface flattening occurs by the annealing at the lower temperature than the case with Ge(111). One of the possible cause of this difference is due to the areal atomic density of hetero-epitaxial Ag surface. In addition, there is a possibility of forming an atomically flat Ag surface over a wide annealing temperature range by optimizing the annealing time.

Then to check the stability of surface flatness, storage time dependence of surface morphology for the Ag/Ge structure was investigated from AFM images as shown in Fig. 4. The samples were stored in vacuum at a pressure of ~10 Pa at room temperature. For the Ag/Ge(100) after annealing at 350 ºC, significant surface roughing at RMS of ~2.6 nm occurs by the storage time for 430 hours. And also, for the Ag/Ge(111) before the annealing, RMS roughness was almost linearly increased with the storage time in the range below ~450 hours, and then saturated at around 3.7 nm. In contrast, for the Ag/Ge(111) with flat surface induced by the annealing at 450 ºC, the increase in the surface roughness with the time was suppressed, and the RMS value remained almost constant at ~0.5 nm after the storage for ~800 hours. Observed surface morphological changes were likely to be due to the thermal migration of Ag atoms, not absorption of contaminant. It is necessary to study the formation of barrier layer to suppress the surface roughing in the future work.

Considering these facts, crystallinity of surface segregated Ge layer was investigated within a few hours after the annealing of Ag/Ge structures. Figures 5 and 6 shows Raman scattering spectra for the hetero-epitaxial Ag/Ge structure measured under the green laser with wavelength of 532 nm. From the reported optical constant of Ag, penetration depth of this green laser in Ag was estimated to be ~13 nm, which was smaller than the thickness of Ag layer as thick as ~100 nm. In other words, the signals originating from the Ge substrate was hardly detected. Note that, a sharp peak of Ge-Ge TO phonon mode at ~300 cm^{-1} originating from the crystalline was clearly observed for the Ag/Ge(111) after the annealing at 450 ºC (Fig. 5). And, a broad signals at 280 cm^{-1} from the amorphous component was hardly detected. In the

case of Ag/Ge(100) after the annealing at temperatures of 300 ºC and 325 ºC (Fig. 6), a peak from crystalline component was also obtained. In addition, spectral background for the sample after the annealing at 300 ºC was gradually increased in the lower region of Raman shift, which indicates the reflection on the sample surface becomes significant probably due to the surface flattening. Comparing the Raman scattering spectra obtained from Ag/Ge(100) and Ag/Ge(111) shown, there was no significant difference in the peak position. These results indicates the ultrathin Ge layer with high crystallinity can be grown on the flat Ag surface by the annealing of both Ag/Ge(100) and Ag/Ge(111) structure.

4. Conclusion

Ultrathin Ge crystal layer growth on the flat hetero-epitaxial Ag surface by the annealing of Ag/Ge(100) and Ag/Ge(111) have been demonstrated. Surface flattening of Ag/Ge(100) can be performed at lower temperature than that of Ge(111). The orientation of ultrathin Ge crystal layer is also controlled by the surface orientation of the Ge substrate.

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References

[1] K. Takeda and K. Shiraishi, Phys. Rev. B **50** (1994) 14916.
[2] M. Ezawa, New J. Phys. **14** (2012) 033003.
[3] M. Kurosawa, et al., Jpn.J. Appl. Phys. **55** (2016) 08NB07.
[4] K. Ito et al., Jpn. J. Appl. Phys., **57** (2018) 06HD08.
[5] J. Yuhara, et. al., ACS Nano, **12** (2018) 11632.
[6] T. B. Massalski, et al, "Binary Alloy Phase Diagrams (American Society for Metals", Materials Park, Ohio, 1986) **1**, pp. 29 and 67.

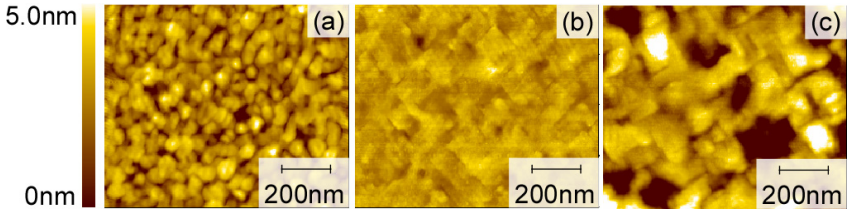

Fig. 1. AFM topographic images of the hetero-epitaxial Ag/Ge(100) taken (a) before and after the annealing at (b) 300 ºC and (c) 400 ºC for 2 hours. Each AFM images was measured by setting the cleaved plane of the Ge(100) substrate at around 45º to the horizontal.

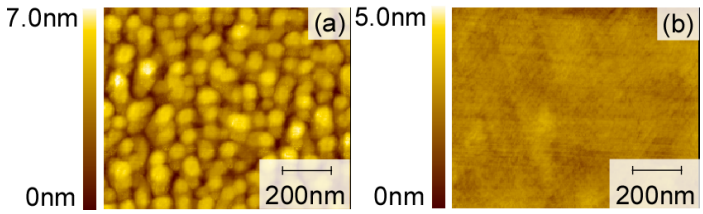

Fig. 2. AFM topographic images of the hetero-epitaxial Ag/Ge(111) taken (a) before and (b) after the annealing at 450 ºC for 2 hours.

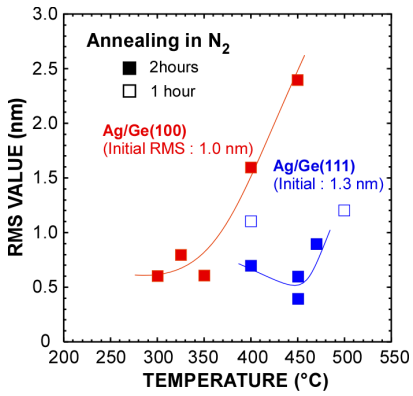

Fig. 3. Temperature dependence of RMS roughness for the samples with the annealing for 2 hours. The results after the annealing for 1 hour were also shown as a reference.

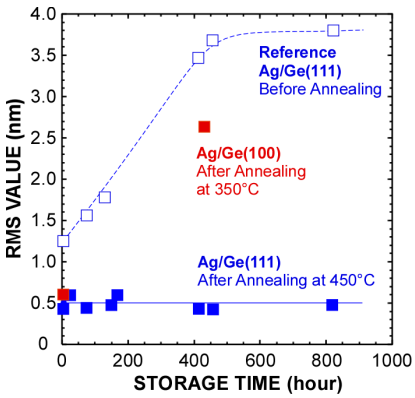

Fig. 4. Storage time dependence of RMS roughness for the hetero-epitaxial Ag on Ge(111) and Ge(100) after the annealing. The results for the Ag/Ge(111) before the annealing was also shown as a reference.

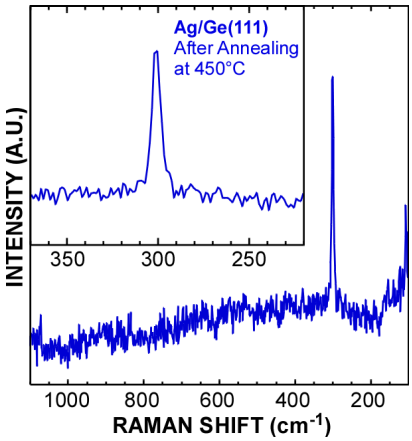

Fig. 5. Raman scattering spectrum taken for the hetero-epitaxial Ag/Ge(111) after the annealing at 450 ºC for 2 hours.

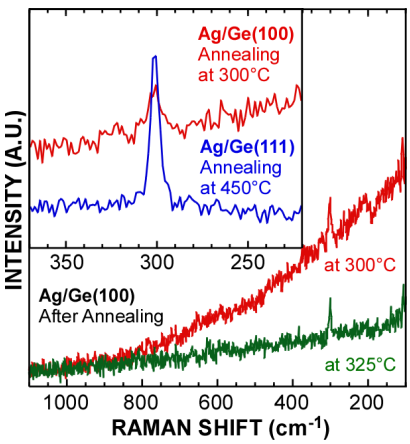

Fig. 6. Raman scattering spectra taken for the hetero-epitaxial Ag/Ge(100) after the annealing at 300 ºC and 325 ºC for 2 hours..