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Growth of 2D Crystal of Group-IV Elements on Epitaxial Ag(111)

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Abstract

We have successfully created the two monolayer-thick two dimensional (2D) crystals of Ge on the epitaxial Ag(111) surface by the thermal annealing of Ag/Ge structure. In this study, surface morphology and chemical structure of epitaxial Ag grown on Si, SiGe, and Ge after the annealing at different temperatures were systematically investigated.

1. Introduction

2D crystals such as silicene and germanene are currently receiving much attention because of its exceptional electronic properties [1, 2]. Recently, silicene (or germanene) was successfully grown by an evaporation of Si (or Ge) atoms on cleaned Ag(111) [3,4] (or Pt(111) [5]) surface at specific substrate temperature. In the previous work [6], we have reported a formation of ultrathin Si or Ge layer as the result of the diffusion of Si or Ge atoms through the 60 nm-thick epitaxial Ag(111) from Si(111) or Ge(111) substrates by an annealing at the temperature over 400 ºC. And, the amount of Ge segregation at Ag surface was found to be larger than that of Si after the same annealing condition. To apply this formation technique to create the 2D crystal, atomicallly flat Ag surface and precise control of Si (or Ge) segregation are required. In this work, to get a clear insight of the relationship between the surface morphology and chemical conposition of Ge/(Si+Ge) of the substrate after the annealing, we have investigated the impacts of thermal annealing on the surface morphology and chemical bonding features at the Ag surface grown on Si(111), $Si_{0.5}Ge_{0.5}$(111) and Ge(111).

2. Experimental Procedure

Three kinds of surface such as Si(111), Ge(111) and $Si_{0.5}Ge_{0.5}$(111) grown on Si(111) were used in this work. The Si(111) surface was wet-chemically cleaned with NH_4OH : H_2O_2 : H_2O = 0.15 : 3 : 7 solution at 80 ºC for 10 min. Subsequently, the Si surface was terminated with hydrogen by dipping in 4.5% diluted HF solution and pure-water rinse. The Ge(111) and $Si_{0.5}Ge_{0.5}$(111) surface were cleaned by dipping in HF solution to remove the surface contaminants and native oxides. After the surface cleaning, a Ag layer with a thickness of around ~100 nm was deposited by thermal evaporation using Ag target at base pressure of 4×10^{-6} Torr. A growth of epitaxial Ag(111) was confirmed from the XRD as shown in Fig. 1. Then, the samples were annealed in N_2 ambience at 450 ºC for 2 hours to enhance the segregation of Si and/or Ge on Ag surface.

3. Results & Discussion

For the AFM images taken for the sample just after Ag(111) growth as shown in Fig. 2, significante differences of the surface morphology and the root-mean-square of surface roughness (RMS) value among the samples were hardly detected. Surface morphology of Ag/Si structure was drastically changed, and RMS value was increased from 2.4 nm to 15.0 nm by the annealing. In contrast, with increasing Ge composition of the substrate, RMS value after annealing was decreased, and very flat surface was obtained for Ag/Ge structure after annealing. Note that, the AFM image for Ag surface on Ge taken after the annealing shows the unique triangular structures (as shown in Figs. 2(f) and 3(a)), which are mainly originating from the crystalline structure at the surface. Moreover, measured AFM line profile between A and B clearly shows step and terrace structure with a step height of ~0.7 nm (as shown in Fig. 3(b)). Chemical bonding features of Ag surface on Ge before and after the annealing were evaluated by using hard x-ray photoemission spectroscopy (HAXPES, hν = 7939eV) as shown in Fig. 4. A spectral shape of Ag $3d_{5/2}$ signals was unchanged after the annealing, which implies that the incorporation of Ge atoms into Ag was below the detection limit of HAXPES analysis (< 0.1 at.%). Ge $2p_{3/2}$ signals were detected after the annealing, and increased with decreasing photoelectron take-off angle from 87º to 40º for the surface sensitive measuerment. These results indicate that Ge atoms were diffused toward the surface through the Ag from Ge surface and exist at Ag(111) surface (as shown in Fig.4(b)). Crystalline structure of this segregated Ge on Ag(111) obtained from the Ag/Ge(111) by annealing at 450 ºC was evaluated from the cross-sectional TEM image as shown in Fig. 5. It was interesting note that there are three layers corresponding to the surface native Ge oxide/segregeted Ge/epitaxial Ag(111) stack, which was in good agreement with the HAXPES analysis as discussed in Fig. 4. Furthermore, we found that an ultra-thin Ge crystal layer in the average thickness of two monolayer was formed on very flat Ag(111) surface.

In summary, this technique of Ge and Si segregation at Ag(111) surface by the annealing is promising to create the 2D crystals.

Acknowledgments

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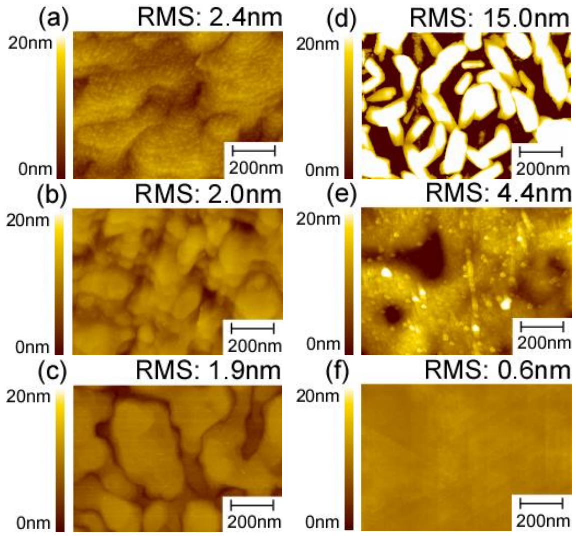

Fig.2 AFM topographic images for the epitaxial Ag(111) surface on (a,d) Si, (b,e) $Si_{0.5}Ge_{0.5}$, and (c,f) Ge taken (a,b,c) before and (d,e,f) after the annealing at temperature of 450 ºC for 2 hours in N_2 ambience.

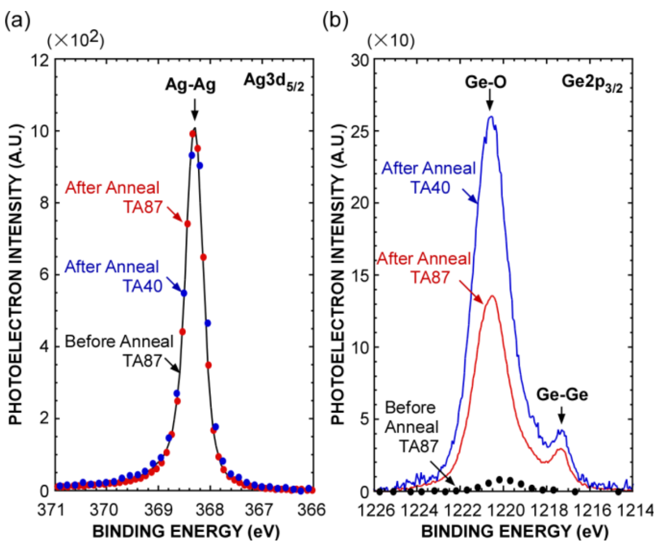

Fig. 4 (a) Ag $3d_{5/2}$ and (b) Ge $2p_{3/2}$ spectra taken for Ag/Ge(111) before and after the annealing. The photoelectron intensity normalization was made by Ag $3d_{5/2}$ signals from the epitaxial Ag layer.

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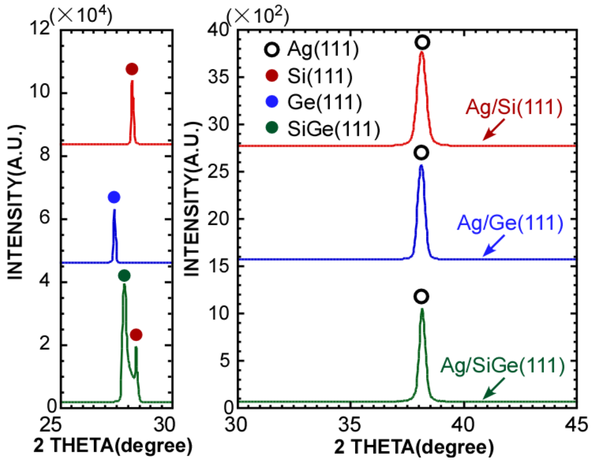

Fig.1 X-ray diffraction pattern of Ag/Si, Ag/Ge and Ag/SiGe/Si.

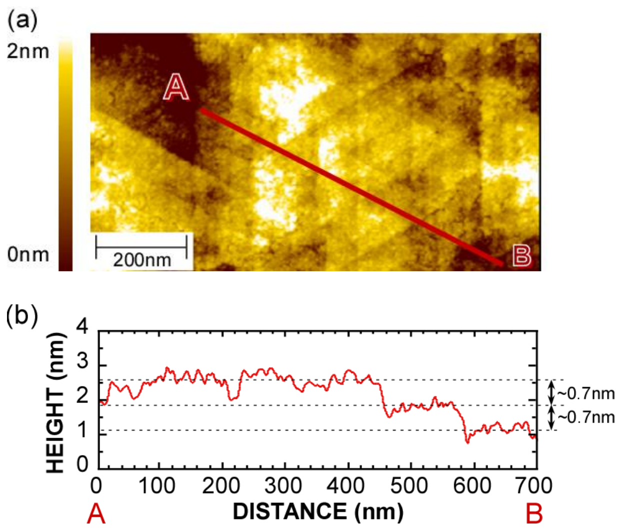

Fig. 3 (a)A AFM image of Ag surface on Ge(111) substrate taken after annealing and (b)a line profile between A and B shown in Fig. 3(a).

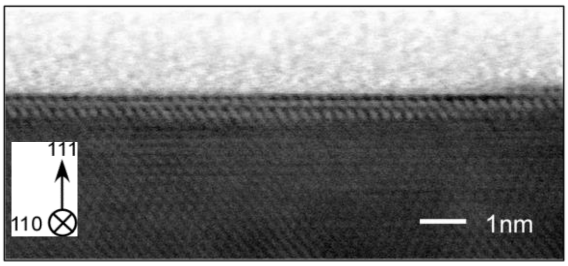

Fig. 5 A cross-sectional TEM image of Ag/Ge structure after the annealing at 450C for 2hours shown in Figs. 3 and 4.