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Evaluation of Si and Ge Segregation from $Si_{0.2}Ge_{0.8}$(111) through Al and Ag Layer

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Abstract

Controls of diffusion and segregation of group IV element (Si, Ge) through a thin metal layer from a stacked structure is one of the effective techniques to grow an ultrathin crystal and a 2D crystal. In this study, a 30 nm-thick Al and Ag layer was deposited on an 85 nm-thick heteroepitaxial $Si_{0.2}Ge_{0.8}$(111) layer, and the surface segregation of Si and Ge atoms by annealing was evaluated by PES and XPS analyses. Segregated Si and Ge on Al surface were covered with Al oxide layer, and oxidation of segregated Ge on Al was hardly detected after annealing.

1. Introduction

Nano-scale ultrathin crystal consisted of Si and Ge has been attracted much attention from the view point of shrinkage of advanced MOSFET devices. Growth techniques for ultrathin and two-dimensional (2D) crystals have been so far investigated. In our previous work, a formation of ultrathin and 2D Ge crystals by annealing of Ag/Ge stacked structure has been demonstrated [1-3]. After the growth of hetero-epitaxial Ag(111) layer on a single crystal Ge(111) substrate by thermal evaporation, Ge atoms were diffused and segregated on the Ag surface by annealing [1, 3]. In addition to the Ge segregation, we found that atomically flat surface was obtained by annealing [3]. This growth method is similar to crystal growth technique by metal induced layer exchange of metal/amorphous staked layer [4], but the crystallographic structure of initial Ge layer is quite different between single crystal and amorphous. In that regard, better understating of segregation mechanism is one of key issues for the control of segregated layer thickness. As for the metal layer, eutectic reaction with Ge is likely to be suitable from the viewpoint of suppression of metal-Ge alloy formation. Based on these results, ultrathin SiGe crystal and/or ultrathin Ge/Si heterostructure could be formed by changing the underlying material from Ge(111) substrate to SiGe(111) layer.

Therefore, in this work, we have studied an impact of annealing on Si and Ge segregation from metal/SiGe/Si structure. Al and Ag were selected as the metal layer because these metals show the eutectic reactions with both Si and Ge [5-8].

2. Experimental Procedure

An epitaxial $Si_{0.2}Ge_{0.8}$(111) layer with a thickness of 85 nm was formed on Si(111) wafer by reduced pressure chemical vapor deposition at 600 ºC using SiH_4-GeH_4 gas mixture with H_2 carrier gas. Subsequently, wet-chemical cleaning of the $Si_{0.2}Ge_{0.8}$(111) surface was carried out by dipping in a 4.5% dilute HF solution and pure water rinse. Then, a 30 nm-thick thin metal layer such as Al or Ag was deposited on the $Si_{0.2}Ge_{0.8}$(111) surface by thermal evaporation with a deposition rate of ~2.5 nm/s at a base pressure of ~1.3×10^{-5} Pa. After that, annealing in N_2 ambient under atmospheric pressure was performed for 30 min to promote the surface segregation of Si and Ge atoms from the $Si_{0.2}Ge_{0.8}$(111) layer through the thin metal layer. The surface morphology was evaluated by AFM. The chemical bonding features were measured by PES or XPS. The take-off angle was set to 90°.

3. Results and Discussion

Surface morphology for the samples taken before and after the 30 nm-thick metal (Al and Ag) deposition on $Si_{0.2}Ge_{0.8}$(111)/Si(111) structure was investigated by AFM measurements (not shown). $Si_{0.2}Ge_{0.8}$(111) surface shows relatively flat surface with root mean square (RMS) roughness of ~0.8 nm. RMS roughness was slightly increased by ~0.1 nm for the samples after both Al and Ag deposition, while some protrusions and rounded shapes were detected. These results indicate the formation of Al and Ag layer with suppression of significant surface roughing.

The chemical bonding features for the Al/$Si_{0.2}Ge_{0.8}$(111) in the region near the surface were evaluated from core-line PES spectra under synchrotron radiation ($h\nu$ = 310.7 eV) as shown in Fig. 1. In each spectrum, the photoelectron intensities and the binding energy were normalized by Al 2p signals from the Al-Al bonding units. The spectral shape of metallic Al 2p signals was unchanged by annealing, which implies that the formation of Al-Si or Al-Ge alloy was below the detection limit of PES analysis (<1 at.%). Al 2p signals from Al oxide were detected for the samples before and after annealing, and its intensity was gradually increased with the temperature. This Al oxide formation was mainly due to surface oxidation by air exposure or residual oxygen in the quartz furnace during annealing. Note that, Si 2p and Ge 3d signals show the increase in the intensities of Si-O and Ge-Ge bonding units with the temperature, indicating that annealing promoted the diffusion and segregation of both Si and Ge atoms. In addition, the oxidation of segregated Si proceeds significantly, as compared to the Ge.

The integrated PES intensities of Si-Si, Si-O, and Ge-Ge bonding units taken for the Al/$Si_{0.2}Ge_{0.8}$(111) structure after annealing at a higher temperature were plotted as a function of annealing temperature as shown in Fig. 2. Since the Al 2p signals from the Al-Al bonding units originated from the

Al layer were hardly detected at the temperature above 500 ºC, these intensities were normalized by the Al 2p signals from the Al-O bonding units. Si 2p signals from the Si-Si and Si-O bonding units were clearly increased with the temperature, which implies that a part of Si-Si bonding units remains probably due to an increase in the surface oxide layer. On the other hand, Ge 3d signals from the Ge-Ge bonding units were decreased. In addition, a slight energy shift of Ge 3d signals corresponding to the SiGe formation so called the chemical shift was observed at a temperature over 500 ºC. From these results, the decrease in the Ge signals with temperature was likely to be due to the increase in the surface oxide thickness and the change in the Ge depth profile.

To get more insights into the Si and Ge segregation, XPS analysis of the ~30 nm-thick Ag/$Si_{0.2}Ge_{0.8}$(111) was also performed under monochromatized Al Kα radiation (hν = 1486.6 eV). Figure 3 shows Ag $3d_{5/2}$, Si 2p, and Ge 3d core-line spectra for the samples before and after annealing, where the photoelectron intensities and the binding energy were normalized by Ag $3d_{5/2}$ signals from the Ag-Ag bonding units. In contrast to the Al/$Si_{0.2}Ge_{0.8}$(111) structure as discussed in Fig. 1, surface segregation of Si and Ge atoms was hardly detected after annealing at 400 ºC. With further increase in the temperature, Si 2p and Ge 3d co-line spectra show not only metallic components (Si-Si and Ge-Ge) but also oxide components (Si-O and Ge-O). Considering the fact that the Al surface is easy to oxidize as compared to the Ag surface, a part of Al oxide was act as a barrier layer of segregated layer against oxidation during annealing as seen in Figs. 1 and 2.

PES intensity of segregated Si and Ge on metal layer shown in Figs. 1-3 was converted as an average thickness using the equations described in references [2, 9]. For the Al/$Si_{0.2}Ge_{0.8}$ after annealing at 600 ºC, the average thickness of Si, Ge, and Si-O was 1.73 nm, 0.95 nm, and 1.95 nm, respectively. For the Ag/$Si_{0.2}Ge_{0.8}$ after annealing at 600 ºC, the average thickness of Si, Ge, Si-O, and Ge-O was 0.16 nm, 0.10 nm, 3.01 nm, and 1.23 nm, respectively. Comparing these results, the average thickness of Si and Ge on Al surface was larger than that on Ag because the segregated layer was covered with Al oxide layer, which indicates good stability of segregated layer against oxidation. In addition, reported solid solubility of Ge in Al is larger than that of Si [5, 6], but obtained average thickness of Ge was thinner than that of Si. This result indicates the Si segregation due to not only the solid solubility of metal layer but also the crystallographic structures such as grain boundaries.

4. Summary

Si and Ge segregation from the hetero-epitaxial $Si_{0.2}Ge_{0.8}$(111) through the ~30 nm-thick Al and Ag layer by annealing have been investigated. For both Al/SiGe and Ag/SiGe structure, amount of Si and Ge segregation was increased with annealing temperature. Segregated Si on Al surface was found to be easily oxidized than that of segregated Ge. The Si and Ge were segregated between the topmost Al oxide and Al layer, and this structure shows good stability against oxidation as compared to that on Ag/SiGe.

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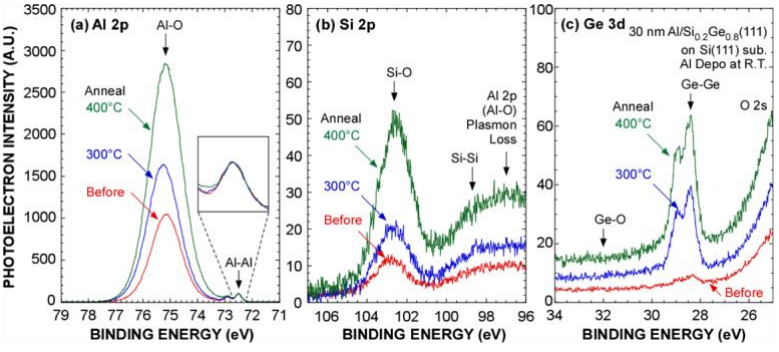

Fig. 1 (a) Al 2p, (b) Si 2p, and (c) Ge3d core-line spectra for the Al/$Si_{0.2}Ge_{0.8}$ before and after annealing for 30 min.

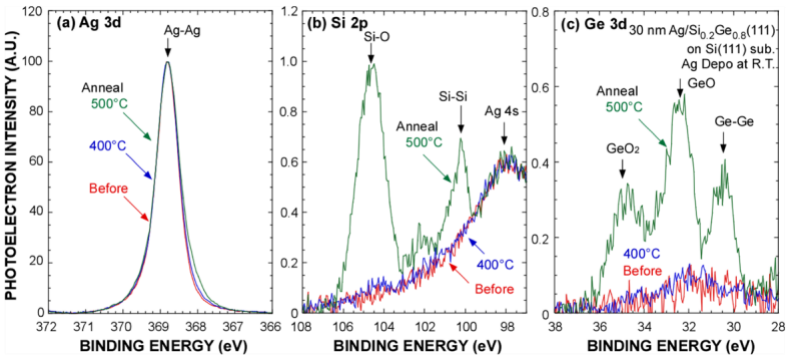

Fig. 3 (a) Ag $3d_{5/2}$, (b) Si 2p, and (c) Ge3d core-line spectra for the Ag/$Si_{0.2}Ge_{0.8}$ before and after annealing for 30 min.

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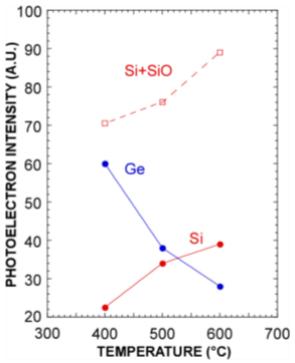

Fig. 2 PES intensities of the Al/SiGe(111) after annealing.