Atomic-order thermal nitridation of group IV semiconductors for ultra-large-scale integration*

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Abstract

One of the main requirements for ultra-large-scale integration (ULSI) is atomic-order control of process technology. Our concept of atomically controlled processing for group IV semiconductors is based on atomic-order surface reaction control in Si-based CVD epitaxial growth. On the atomic-order surface nitridation of a few nm-thick Ge/about 4 nm-thick Si₀.₅Ge₀.₅/Si(100) by NH₃, it is found that N atoms diffuse through nm-order thick Ge layer into Si₀.₅Ge₀.₅/Si(100) substrate and form Si nitride, even at 500 °C. By subsequent H₂ heat treatment, although N atomic amount in Ge layer is reduced drastically, the reduction of the Si nitride is slight. It is suggested that N diffusion in Ge layer is suppressed by the formation of Si nitride and that Ge/atomic-order N layer/Si₁₋ₓGeₓ/Si (100) heterostructure is formed. These results demonstrate the capability of CVD technology for atomically controlled nitridation of group IV semiconductors for ultra-large-scale integration.

Keywords: nitridation, Ge, Si, atomically controlled processing, chemical vapor deposition, ULSI

Mathematics Subject Classification: 2.07, 5.01, 6.00

1. Introduction

Atomically controlled processing has become indispensable for the fabrication of Si- and Ge-based ultra-small devices and heterodevices for ultra-large-scale integration because high performance devices require atomic order abrupt heterostructures and doping profiles as well as strain engineering due to introduction of Ge into Si. Our concept of atomically controlled processing is based on atomic-order surface reaction control in Si-based chemical vapor deposition (CVD) growth [1–5]. Introduction of N atomic layer at the interface between the high-k dielectric and the channel has been employed to suppress the interface trap formation [6]. Additionally, the insertion of N atomic layer within the channel may be beneficial for high mobility channel formation [3, 7]. Nevertheless, the goal is to create group IV semiconductors with high mobility as well as high carrier concentration by strain control for ULSIs using atomically controlled processing. Self-limiting formation of 1–3 atomic layers of group IV or related atoms in the thermal adsorption and reaction of hydride gases (SiH₄, GeH₄, NH₃, PH₃, B₂H₆, CH₄ and SiH₃CH₃) on Si(100), Si₀.₅Ge₀.₅(100) or Ge(100) at the temperature below around 500 °C were generalized based on the Langmuir-type model [1, 3, 5]. In many cases, hydride molecules are adsorbed and react simultaneously on the surface, as shown in figure 1 [3, 5]. Moreover, atomic-layer doping was performed by Si or Si₁₋ₓGeₓ epitaxial growth on N [3, 7, 8], P [3, 5, 9, 10], B [11], C [5, 12], Si [10] atomic layer already-formed on Si or Si₁₋ₓGeₓ surface. Especially, atomic layer doping of P and B in Ge epitaxial growth was performed at 300 °C.

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In this paper, atomic-order surface nitridation of a few nm-thick Ge/about 4 nm-thick Si$_{0.5}$Ge$_{0.5}$/Si(100) by NH$_3$ is reviewed. Furthermore, the N and Si behaviors in the layers are discussed.

2. High quality Ge epitaxial growth on Si$_{0.5}$Ge$_{0.5}$/Si(100) substrate and nitridation by NH$_3$

High quality Ge/Si$_{0.5}$Ge$_{0.5}$/Si(100) heteroepitaxial growth and nitridation by NH$_3$ were performed using an ultraclean hot-wall low-pressure CVD system shown in figure 2 [1, 3]. Details of the system have been described elsewhere [1, 3]. Before loading the Si (100) wafers into the reactor, they were cleaned for several cycles in a 4:1 solution of 96% H$_2$SO$_4$ and 30% H$_2$O$_2$, high-purity deionized water, and 1–2% HF with a final rinse in deionized water. The typical process sequence for the Ge/Si$_{0.5}$Ge$_{0.5}$/Si(100) heteroepitaxial growth is shown in figure 3. After loading of the wafers, they are heat-treated at 750 °C in a H$_2$ environment and about 4 nm-thick Si buffer layer was epitaxially grown in a SiH$_4$–H$_2$ gas mixture at 600 °C to obtain a clean Si surface. After that, about 4 nm-thick Si$_{0.5}$Ge$_{0.5}$ layer and were epitaxially grown on the substrate at 450 °C in a SiH$_4$–GeVH$_4$–H$_2$ gas mixture. Removing hydrogen termination on the Si$_{0.5}$Ge$_{0.5}$ surface, a few nm-thick Ge epitaxial growth was performed at 350 °C in a GeH$_4$–He–Ar gas mixture. After unloading the samples, they were nitrided for 30 min at NH$_3$ partial pressure 250 Pa and 500–600 °C in a NH$_3$–Ar mixture using the other ultraclean hot-wall low-pressure CVD system. Before the nitridation, the samples were heat-treated at 600 °C in a H$_2$ environment of pressure 60 Pa in order to remove the native oxide on the Ge surface because Ge surface is native-oxidized in clean room air. After the nitridation, some samples were heat-treated in a H$_2$ environment of pressure 60 Pa in order to investigate the reduction of the nitrided films.

The amounts of Ge, Si and N atoms for the films were calculated from the intensity of Ge 3d, Si 2p and N 1s measured by x-ray photoelectron spectroscopy (XPS). The binding energies of the fundamental peaks Ge 3d5/2 and Si 2p3/2 were assumed to be 29 eV and 99 eV, respectively. The separation between the XPS intensity from Ge surface and that inside Ge/Si$_{0.5}$Ge$_{0.5}$ layers is dependent on the take-off angle of photoelectron detection. Because the ratio of the XPS intensity from the Ge surface and to that inside the Ge/Si$_{0.5}$Ge$_{0.5}$ layers is dependent on the take-off angle of photoelectron detection, the intensity inside Ge/Si$_{0.5}$Ge$_{0.5}$ layers is separated from that at Ge surface. The XPS Si 2p spectra of take-off angle 90° and 55° are shown in figure 4. It is found that the Si 2p peaks of oxidized Si at the Ge surface [16] and of nitrided Si [17] inside the Ge/Si$_{0.5}$Ge$_{0.5}$ layers appear at 102.2 eV and 101.2 eV, respectively. By the similar way, it was found that the Ge 3d peaks of the oxidized Ge at the Ge surface [16, 18] and of the nitrided Ge [13, 19] inside the Ge/Si$_{0.5}$Ge$_{0.5}$ layers appear at 32.1 eV and 30.9 eV, and the N 1s
peak at the Ge surface and inside the Ge layer at 397.1 eV. From these peak intensities, N atomic amount inside Ge layer is evaluated. Thicknesses of Ge and Si$_{0.5}$Ge$_{0.5}$ layers selectively-grown on partially SiO$_2$ covered Si (100) substrate were measured by atomic force microscopy and cross sectional transmission microscopy (TEM).

3. N diffusion into Ge layer and nitridation of Si through Ge layer

As shown in figure 4, Si oxide is observed at the Ge surface and Si nitride is formed inside the Ge surface. These results suggest that Si atoms diffuse into Ge surface from Si$_{0.5}$Ge$_{0.5}$/Si substrate and N atoms diffuse into Si$_{0.5}$Ge$_{0.5}$/Si substrate from Ge surface. It was found that the segregation of atomic-layer Si at Ge surface occurs self-limitedly even only by the heat treatment of 500 °C. In the case of nitridation at 350–400 °C and subsequent Ar or H$_2$ heat treatment of 400–700 °C, it was reported that N atomic amount on Si (100) and Si$_{0.5}$Ge$_{0.5}$(100) surfaces is scarcely changed, but that on Ge (100) surface tends to decrease with increasing the heat treatment temperature [13, 14] and that N atomic amounts of 3×10$^{14}$ cm$^{-2}$ and 6×10$^{14}$ cm$^{-2}$ are confined within 1 nm- and 1.5 nm-thick regions for Si epitaxial growth at 500 °C [3, 7] and Si$_{1-x}$Ge$_x$, at 450 °C, [8] respectively, and it was suggested that N atoms bound to Ge atoms tend to be transferred to Si atoms at temperatures above 400 °C [8, 13–15].

The results for nitridation of Ge layer are largely different from those of Si and Si$_{1-x}$Ge$_x$.

The XPS spectra of N 1 s, Ge 3d, and Si 2p for about 2.5 and 30 nm-thick Ge/about 4 nm-thick Si$_{0.5}$Ge$_{0.5}$/Si(100) nitrided at 600 °C with and without subsequent H$_2$ heat treatment are shown in figures 5–7, respectively. In these figures, the signals which indicate the oxidation at the surface are mainly included. Especially, the oxidation of Ge surface strongly depends on humidity and exposure time in the clean room air before XPS measurement and Ge oxide is reduced by Si at very low temperature such as 300 °C [16]. In figures 5 and 6, the N 1 s peak and the chemical shifted Ge peak which show Ge–N bonds from the inside of 30 nm-thick Ge/Si$_{0.5}$Ge$_{0.5}$/Si (100) nitrided is lower and higher than those for 2.5 nm-thick Ge/Si$_{0.5}$Ge$_{0.5}$/Si (100), and almost disappears by H$_2$ heat. It should be noted that the Si$_{0.5}$Ge$_{0.5}$ layer and Si nitride are not detected for the 30 nm-thick sample because the thickness is much larger than the electron escape depth of XPS. From the ratio of the chemical shifted Ge integrated intensity at Ge–N peak to the Ge integrated intensity except for Ge–O peak, the average nitrided Ge concentration of the 2.5 nm-thick and 30 nm-thick samples is estimated to be about 2×10$^{21}$ cm$^{-2}$ for nitridation at 600 °C and about 3×10$^{20}$ cm$^{-2}$ after H$_2$ heat treatment at 600 °C. For nitridation at 500 °C, treatment, while the N 1 s peak for 2.5 nm sample does not disappear, the average nitrided Ge concentration was nearly the same as that of 600 °C. Therefore, it is clear that N atoms diffuse into Ge layer over nm-order depth, even at 500 °C. In the
2.5 nm-thick sample, the Si nitride inside the Ge/Si\textsubscript{0.5}Ge\textsubscript{0.5} layers is formed by nitridation and the reduction of the Si nitride is not enough performed by H\textsubscript{2} heat treatment as shown in figure 7. Assuming that the Si nitride is formed at the interface between Ge and Si\textsubscript{0.5}Ge\textsubscript{0.5} layers and that the photoelectron escape depth is 2.1 nm in Si and Ge, the nitrided Si atomic amounts at the interface are about 1.2 × 10\textsuperscript{15} cm\textsuperscript{-2} (about two atomic-layers) for nitridation at 600 °C and 5 × 10\textsuperscript{14} cm\textsuperscript{-2} (about one atomic-layer) at 500 °C. By H\textsubscript{2} heat treatment at 600 °C, the amount of the nitride Si formed at 600 °C decreases to about 9 × 10\textsuperscript{14} cm\textsuperscript{-2}. In the present samples, the ratio of the total N atomic amount calculated from N 1 s intensity to the sum amount of chemical shifted Ge and Si (Ge and Si atomic amounts) is about 1.3 with a data fitting error of 30%. This may mean that there are Ge\textsubscript{3}N\textsubscript{4} and Si\textsubscript{3}N\textsubscript{4} in the samples. The cross sectional high-resolution TEM images are shown in figure 8. The crystallinity of Ge/Si\textsubscript{1-x}Ge\textsubscript{x}/Si(100) heterostructure is scarcely changed by nitridation due to NH\textsubscript{3} and subsequent H\textsubscript{2} heat treatment [20]. These results suggest that N atoms diffuse through nm-order thick layer into Si\textsubscript{0.5}Ge\textsubscript{0.5}/Si(100) substrate and form Si nitride, and by subsequent H\textsubscript{2} heat treatment, Ge/atomic-order N layer/Si\textsubscript{1-x}Ge\textsubscript{x}/Si (100) heterostructure is formed.
4. Conclusion

On the atomic-order surface nitridation of a few nm-thick Ge/ about 4 nm-thick Si$_{0.5}$Ge$_{0.5}$/Si(100) by NH$_3$, N atoms diffuse through nm-order thick Ge layer into Si$_{0.5}$Ge$_{0.5}$/Si(100) substrate and form Si nitride even at 500 °C. By subsequent H$_2$ heat treatment, although N atomic amount in Ge layer is reduced drastically, the reduction of the Si nitride is slight. It is suggested that N diffusion in Ge layer is suppressed by the formation of Si nitride and that Ge/atomic-order N layer/Si$_{1-x}$Ge$_x$/Si (100) heterostructure is formed. These also support that Si layer in Ge becomes a barrier of impurity diffusion [21].

These results demonstrate the capability of CVD technology for atomically controlled nitridation of group IV semiconductors for ultra-large-scale integration.

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Figure 8. Cross sectional high resolution TEM images for about 7 nm-thick/about 4 nm-thick Si$_{0.5}$Ge$_{0.5}$/Si (100) (a) nitrided for 30 min at 600 °C and (b) subsequently heat-treated for 30 min at 600 °C in H$_2$ environment.