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Annealing effects on Ge/SiO_2 interface structure in wafer-bonded germanium-on-insulator substrates

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1. Introduction

Germanium-on-insulator (GOI) attracts much attention because of higher electron- and hole- mobility in Ge than that in Si already applied as silicon-on-insulator (SOI) substrates. Many techniques have been proposed to fabricate GOI structures such as wafer bonding [1], seeding lateral liquid-epitaxy [2], and condensation technique. A wafer bonding technique using both Si wafer covered with SiO_2 layers and Ge wafer with high crystallinity is advantageous to fabricate GOI substrates with high-quality Ge layers in a wafer scale [3]. Chemical bonds at Ge/SiO_2 interfaces are achieved by annealing in this technique. However, there is a lack of fundamental understanding of the annealing effects on structural property at the Ge/SiO_2 interfaces on the atomic to nanometer scales although controls of the interface structure is crucial to obtain desirable electronic states at the interface.

In this study, we investigated annealing effects on the Ge/SiO_2 interface structure in wafer-bonded GOI substrates in the temperature range between 500°C and 800°C using transmission electron microscopy (TEM) and a combination scheme of scanning TEM (STEM) and electron energy-loss spectroscopy (EELS).

2. Experimental

3-inch Si (001) and Ge (001) wafers were used for the fabrication of GOI substrates. Surfaces of Ge (001) and Si (001) wafers with SiO_2 layers of 400 nm in thickness were treated with a solution of $NH_4OH : H_2O = 1 : 1$ for 10 min and rinsed in deionized water for 10 min. The wafer surfaces of Ge and SiO_2 were contacted each other in a clean room at room temperature. Preliminary annealing of the pairs of contacted wafers was carried out at 300°C for 1 h in a N_2 atmosphere of 2 Pa. Then, Ge sides of the bonded wafers were thinned to 200 nm by the machine polishing. Finally, the bonded wafers were annealed at temperatures of 500°C, 600°C, 700°C and 800 °C for 1 h in vacuum at a pressure of 10^{-3} Pa to make strong bonding at the Ge/SiO_2 interfaces. Structural analysis of Ge/SiO_2 interfaces was performed by cross-sectional and plan-view TEM. A STEM-EELS was also applied to chemical analysis at the Ge/SiO_2 interfaces.

3. Results

Figures 1(a)–1(d) show cross-sectional TEM images of the Ge/SiO_2 interfaces in GOI substrates after the annealing at 500°C, 600°C, 700°C and 800°C, respectively. As indicated by arrows in Figs. 1(a)–1(c), nanometer-sized hemispherical amorphous objects were observed at the Ge/SiO_2 interfaces. We confirmed that the density of the hollows were quite small after the annealing at 700°C in comparison to that after the annealing at 500°C and 600°C by both the cross-sectional and plan-view TEM observations. From the cross-sectional TEM images of the Ge/SiO_2 interfaces after the annealing at 500°C, 600°C and 700°C (Fig. 1(a)–1(c)), it is found that the depth of hollows is estimated to be 2.9–3.4 nm (± 1 nm) independently on annealing temperature. Flat interfaces are formed after the annealing at 800°C (Fig. 1(d)).

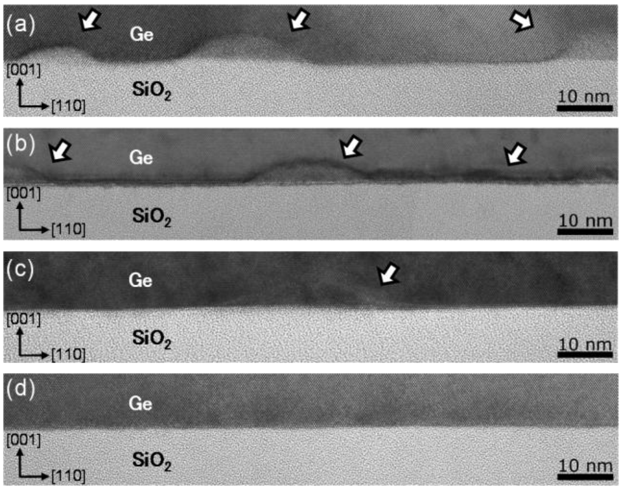

Fig. 1 Cross-sectional TEM images of the Ge/SiO_2 interfaces in GOI substrates after annealing at 500°C in (a), 600°C in (b), 700°C in (c) and 800°C in (d). The arrows depict the hollows of Ge substrates.

To identify chemical species of the hollows, STEM-EELS analysis was performed using a fine electron probe. EELS spectra around an energy-loss region of Ge-$L_{2,3}$ were acquired across the hollows and flat Ge/SiO_2 interface as shown in an annular dark-filed (ADF)-STEM image (Fig. 2(a)), where the acquisition positions are indicated by circles. Figure 2(b) depicts a series of EELS spectra after the background subtraction by the conventional method. The intensity of Ge-$L_{2,3}$ edges varies abruptly at the Ge/SiO_2 interface in Fig. 2(c) whereas the intensity increase gradually across the interface as in Fig. 2(b). This result indicates that Ge concentration within the hollow is smaller than that of the Ge substrate. The O-K edges are also detected in the hollows (not shown here), which suggests the hollows are amorphous Si–Ge oxides. An EELS spectrum including Si-$L_{2,3}$ and Si-L_1 edges acquired at the hollow is also depicted in Fig. 2(d) with the reference EELS spectrum of amorphous SiO_2 [4]. Figure 2(d) indicates not only the presence of Si atoms in the hollow but also the presence of chemical bonding states between Si and O atoms, Si-O which is quite similar with that of amorphous SiO_2. Consequently, the hollows are considered to be amorphous Si-rich $Si_{1-x}\,Ge_xO_2$ from both TEM and STEM-EELS results although it is difficult to estimate x value within this experiment.

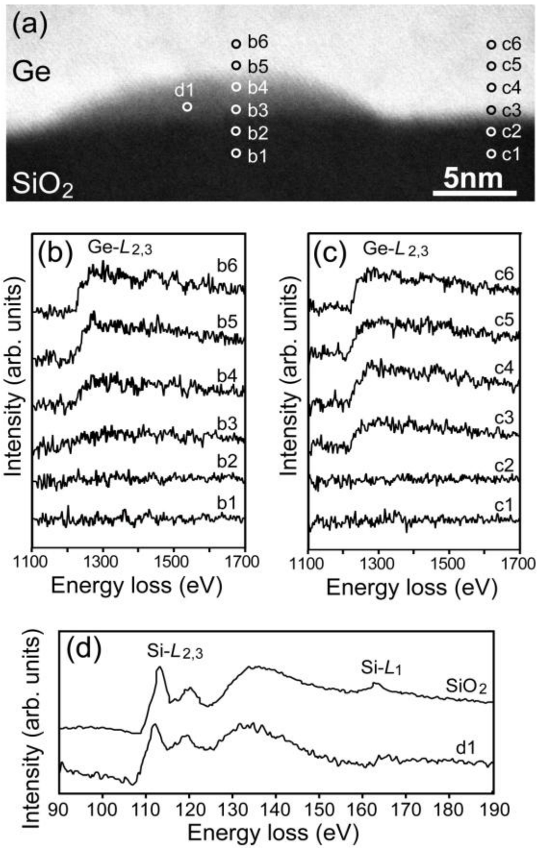

Fig. 2. ADF-STEM image of the hollow of Ge at the Ge/SiO_2 interface in the GOI substrate. (b and c) EELS spectra including Ge-$L_{2,3}$ edges acquired at the positions of b1–b6, (b) and c1–c6, (c) indicated by circles in (a). (d) EELS spectrum including Si-$L_{2,3}$ and Si-L_1 edges acquired at the position of d1 indicated in (a) and the reference spectrum of amorphous SiO_2 [4].

4. Discussion

The mechanism of formation and absence of the hollows at the Ge/SiO_2 interfaces can be explained by two kinds of diffusion events of oxygen species. One is lateral diffusion along the Ge/SiO_2 interface and the other is vertical diffusion toward the surfaces of Ge substrates. After the preliminary annealing at 300°C, native oxide-layers of GeO_2 should exist at the Ge/SiO_2 interface because the surfaces of Ge substrates are covered with native oxide-layers of GeO_2 [5]. As GeO_2 decomposes at 420°C [6], the generation of movable oxygen species occurs at the Ge/SiO_2 interfaces in the temperature ranges between 500°C and 800°C. The oxygen species can diffuse both along the Ge/SiO_2 interfaces and toward surfaces of Ge substrates. Although both diffusion events occur simultaneously, lateral diffusion along the Ge/SiO_2 interface is dominant at 500°C and 600°C, resulting in the formation of the number of hollows of the amorphous oxides. Agglomeration of the oxygen species decrease areas of unstable interface. Interdiffusion of Si atoms in SiO_2 layers and Ge atoms also occurs to form Si-rich $Si_{1-x}\,Ge_xO_2$ hollows. At 700°C and 800°C, it is deduced that most of oxygen species diffuse toward the outside of Ge substrates without formation of the amorphous hollows.

3. Conclusions

Annealing effects on Ge/SiO_2 interface structure in GOI substrates were investigated by TEM and STEM-EELS. Nanometer-sized amorphous hollows was observed at the Ge/SiO_2 interfaces after annealing at 500°C and 600°C whereas the density of the hollows was very small after annealing at 700°C and 800°C. The hollows are attributed to amorphous oxides of Si-rich $Si_{1-x}\,Ge_xO_2$. Formation and absence of the amorphous hollows can be explained by two types of diffusion events of oxygen species which occur at the Ge/SiO_2 interface.

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