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Insight into unusual impurity absorbability of GeO$_2$ in GeO$_2$/Ge stacks

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Adsorbed species and its diffusion behaviors in GeO$_2$/Ge stacks, which are future alternative metal-oxide-semiconductor (MOS) materials, have been investigated using various physical analyses. We clarified that GeO$_2$ rapidly absorbs moisture in air just after its exposure. After the absorbed moisture in GeO$_2$ reaches a certain limit, the GeO$_2$ starts to absorb some organic molecules, which is accompanied by a structural change in GeO$_2$ to form a partial carbonate or hydroxide. We also found that the hydrogen distribution in GeO$_2$ shows intrinsic characteristics, indicative of different diffusion behaviors at the surface and at the GeO$_2$/Ge interface. Because the impurity absorbability of GeO$_2$ has a great influence on the electrical properties in Ge-MOS devices, these results provide valuable information in realizing high quality GeO$_2$/Ge stacks for the actual use of Ge-MOS technologies. © *2011 American Institute of Physics*. [doi:10.1063/1.3644393]

Germanium (Ge) is one of the most promising candidates as advanced channel materials of metal-oxide-semiconductor (MOS) devices because of its higher carrier mobility than silicon (Si).[1] However, since GeO$_2$, which is a fundamental dielectric for Ge-MOS just like SiO$_2$ in Si complementary MOS, has the characteristics of thermal instability and water solubility,[2,3] Ge-MOS devices have been unsuccessful in practical use. It is also known that an unfavorable phenomenon of GeO volatilization at the GeO$_2$/Ge interface during the high temperature (over 600 °C) processing of MOS transistors leads to a serious deterioration of the Ge-MOS.[4] Therefore, one of the most important issues concerning Ge-MOS technologies has been the formation of a high quality dielectric on the Ge-channel. Recently, theoretical studies showed that a low interface defect (Ge dangling bond) was obtained for the GeO$_2$/Ge interface due to its viscoelastic properties,[5,6] and some experimental studies demonstrated good electrical properties of the Ge-MOS.[7–10] For example, Hosoi *et al.* reported that the electrical properties of Ge-MOS capacitors could be improved by *in situ* vacuum annealing at 300 °C prior to metal gate electrode deposition, and an increase in the inversion capacitance, depending on its air exposure time, could be suppressed by an Al$_2$O$_3$ layer capped on the GeO$_2$ surface.[8] Meanwhile, Kutsuki *et al.* reported that surface nitridation on ultrathin GeO$_2$ was an effective way to improve the electrical properties (drastic suppression of leakage current, etc.) compared to the GeO$_2$/Ge stacks,[9] inferring that the nitride (Ge$_3$N$_4$) film on GeO$_2$ works as a barrier layer against the chemical reaction of GeO$_2$ with air. These studies might indicate that the impurity absorbability of GeO$_2$ strongly affects the electrical properties of Ge-MOS capacitors. However, the relationship between the electrical and physical properties of the Ge-MOS has not been fully understood. The physical origin of the improved electrical properties of Ge-MOS described in the previous study (Refs. 8 and 9) must be clarified for the development of advanced Ge-based devices.

In this study, we have investigated the adsorbed species and their diffusion behaviors in GeO$_2$/Ge stacks from the viewpoint of the influence of air exposure and the impact of vacuum annealing at 300–400 °C. Especially, the hydrogen distribution in GeO$_2$, which seems to strongly affect the electrical properties of the Ge-MOS, has been further clarified.

P-type Ge (100) substrates were cleaned by cyclic treatment using diluted HF and ultrapure water. GeO$_2$ dielectric films (20-30 nm) were fabricated by dry oxidation at 550 °C for 4-6 h using a conventional furnace. The GeO$_2$/Ge stack samples were exposed to air (temperature: 20-25 °C, humidity: 40-50%) for 7 days or annealed at 300 °C for 30 min under a vacuum of 6×10^{-4} Pa. Since the samples after the dry oxidation and the vacuum annealing were exposed to air during the sample transfer, it was difficult to identify the impurity concentrations of the as-oxidized sample due to its hygroscopic property. Thus, we considered the vacuum-annealed GeO$_2$ as a reference and compared its physical property with that of GeO$_2$ after air exposure for 7 days. The absorbed species in the GeO$_2$ were characterized by Fourier transform infrared spectroscopy (FT-IR). The amount of absorbed moisture in the GeO$_2$, when exposed to air for 7 days, was quantified by temperature programmed desorption mass spectrometry (TPD-MS). The adsorbed organic molecules on the GeO$_2$ and depth profiles of the impurities in the GeO$_2$ were investigated by static (time-of-flight: TOF) secondary ion mass spectrometry (SIMS) and dynamic SIMS, respectively. To further investigate the diffusion kinetics of the impurities in the GeO$_2$ focusing on the reaction between the GeO$_2$ and moisture (H$_2$O) in the air, the annealed samples at 300 °C for 30 min under vacuum were exposed to saturated D$_2$O (heavy water) moisture in an N$_2$ atmosphere (temperature: 20-25 °C, humidity: 80-90%) with no air exposure (by means of the transferring in an inert gas). The reason why we used D$_2$O instead of H$_2$O was to distinguish the hydrogen (deuterium) of the moisture from that of organic contamination. The depth profiles of the deuterium in the GeO$_2$ for different D$_2$O moisture exposure times were obtained by dynamic SIMS.

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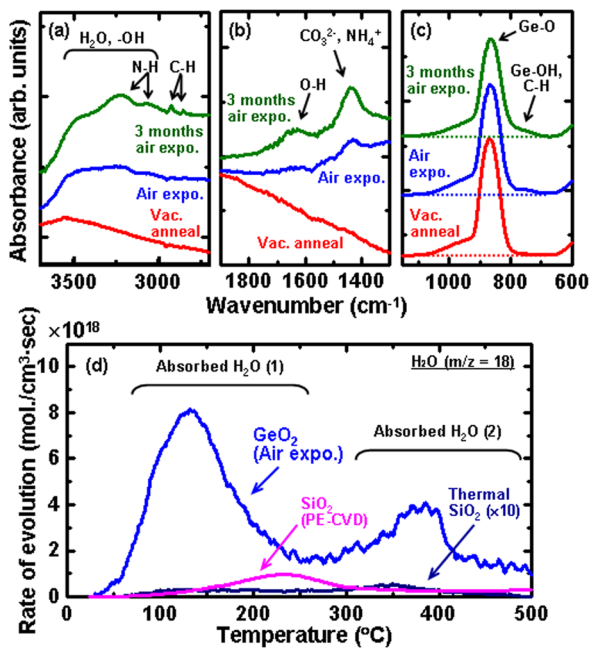b)Electronic mail: hosoi@mls.eng.osaka-u.ac.jp.

FIG. 1. (Color online) (a)–(c) FT-IR absorption spectra of GeO_2 after air exposure for 3 months (3 months air expo.), after air exposure for 7 days (air expo.), and after 300 °C vacuum annealing (vac. anneal). (d) Moisture desorption curves of GeO_2 (air expo.) and SiO_2 (PE-CVD and thermally grown; see Ref. 12) obtained from TPD-MS. Absorbed H_2O (2) is assigned to confined H_2O in GeO_2.

Figures 1(a)–1(c) show the FT-IR absorption spectra of GeO_2 after air exposure for 7 days (air expo.) and after 300 °C vacuum annealing (vac. anneal). To emphasize the influence of the air exposure, the result of the GeO_2 after air exposure for 3 months (3 months air expo.) is also shown in Figs. 1(a)–1(c). The absorption of moisture and organic molecules (N-H and C-H groups, etc.) as well as the formation of carbonate (including ammonium salt) and hydroxide in GeO_2 were observed after air exposure for 7 days but not observed after 300 °C vacuum annealing. These amounts showed a clear increase with the air exposure time, which is a peculiar phenomenon of GeO_2 unlike SiO_2. Fig. 1(d) shows the moisture desorption curve of GeO_2 after air exposure for 7 days and that of SiO_2 (Ref. 11) formed by two different processes [plasma enhanced chemical vapor deposition (PE-CVD) and thermally grown]. The amount of moisture absorption by GeO_2 was around one order of magnitude higher than that by SiO_2. These results revealed that GeO_2 has the characteristic of an unusual absorbability of moisture and organic molecules in air, which suggesting the possible origin for the electrical deterioration of Ge-MOS devices by air exposure as described in Ref. 8.

Figure 2 shows the relative intensities of various secondary ion peaks in the TOF-SIMS spectra of GeO_2 after air exposure for 7 days and GeO_2 after 300 °C vacuum annealing. In order to compare GeO_2 with SiO_2, the results of the native SiO_2 (Ref. 12) [SiO_2 (air expo.)] are also shown in Fig. 2. The TOF-SIMS results show that no specific molecules exist on the GeO_2 compared to SiO_2. On the other hand, some molecules ($^{18}NH_4^+$, etc.) on GeO_2 after 300 °C vacuum annealing were lower than that on GeO_2 after air exposure for 7 days.

To investigate the depth profiles of impurities (hydrogen, carbon, and nitrogen) in GeO_2, dynamic SIMS analyses were
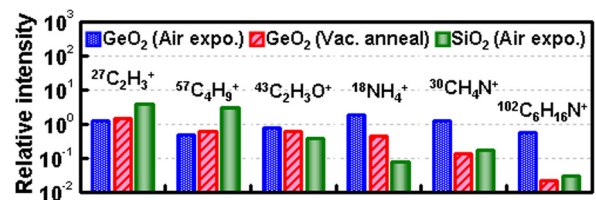

FIG. 2. (Color online) Relative intensities of various secondary ion peaks in TOF-SIMS spectra of GeO_2 after air exposure for 7 days (air expo.), after 300 °C vacuum annealing (vac. anneal), and native SiO_2 [SiO_2 (air expo.); see Ref. 14]. Intensities of the ion peaks of GeO_2 and SiO_2 are normalized by $^{74}Ge^+$ and $^{30}Si^+$, respectively.

carried out for GeO_2 after air exposure for 7 days and GeO_2 after 300 °C vacuum annealing, as shown in Figure 3. The concentration of each impurity in GeO_2 after 300 °C vacuum annealing was lower than that in GeO_2 after air exposure for 7 days. Although carbon and nitrogen were distributed near the surface of the GeO_2, hydrogen was distributed throughout the GeO_2 layer. Moreover, the hydrogen concentration in GeO_2 gradually increased toward the GeO_2/Ge interface. These results suggest the different diffusion behavior of hydrogen from that of carbon and nitrogen.

Thus, we investigated the diffusion kinetics of the impurities in GeO_2 under a humid atmosphere. Figures 4(a) and 4(b) show SIMS depth profiles of deuterium and carbon for different D_2O moisture exposure times (0.1, 1, 10, and 60 min). It is noted that the reaction between the moisture and GeO_2 was intentionally accelerated by exposing GeO_2 to a high humidity D_2O atmosphere (80-90%). Fig. 4(a) revealed that deuterium rapidly diffuses into the GeO_2 just after the D_2O exposure, and the deuterium concentration increased with the D_2O exposure time. On the other hand, carbon does not diffuse into GeO_2 for at least 10 min, but the carbon concentration in GeO_2 drastically increased after a 60-min exposure. Fig. 4(c) shows the D_2O exposure time versus the deuterium, carbon, and germanium intensity at a 10-nm depth. Because the deuterium concentration in GeO_2 is proportional to the square root of time, the distribution of deuterium, representing hydrogen derived from moisture, is subject to a diffusion process in GeO_2 from the air, which has a diffusion coefficient according to Fick's second law.[13]
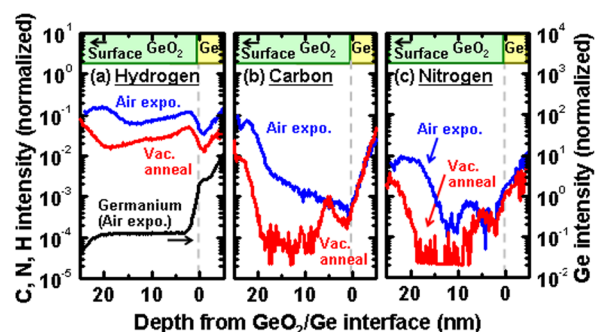

FIG. 3. (Color online) SIMS depth profiles of (a) hydrogen, (b) carbon, and (c) nitrogen in GeO_2 after air exposure for 7 days (air expo.) and after 300 °C vacuum annealing (vac. anneal). Horizontal axis (depth) was shown on the basis of GeO_2/Ge interface determined from Ge profile in Fig. 3(a) and vertical axis (secondary ion intensities) was normalized by oxygen at each depth point. The SIMS intensities of the impurities within the Ge substrate are artifact caused by the normalization method.
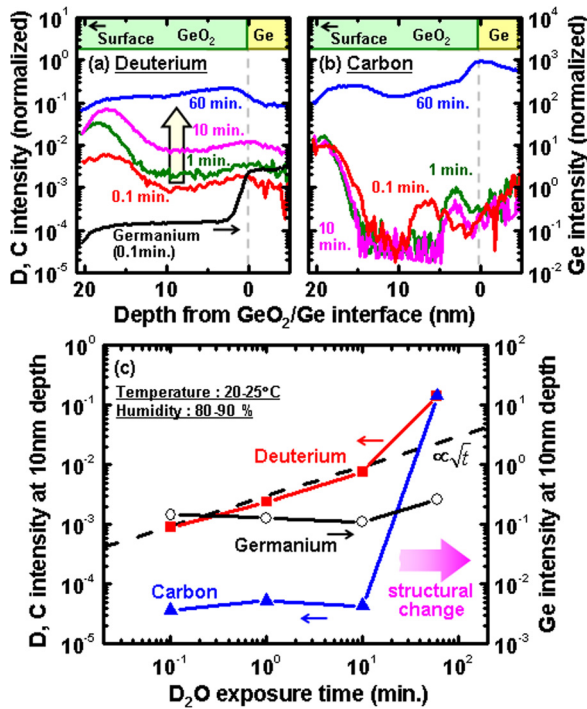
FIG. 4. (Color online) SIMS depth profiles of (a) deuterium and (b) carbon in GeO_2 films for different D_2O moisture exposure times of 0.1, 1, 10, and 60 min. Spectrum calibration is the same as that in Fig. 3. (c) Intensities of deuterium, carbon, and germanium at 10-nm depth depending on the D_2O exposure time.

After the D_2O exposure for 60 min, the deuterium, carbon and germanium drastically increased. These results revealed that when the hydrogen concentration in GeO_2 has reached a certain limit, GeO_2 starts to absorb a lot of impurities (carbon, etc.) along with some structural changes.

Finally, the diffusion distribution of hydrogen in GeO_2 was measured in detail. Figure 5(a) shows the depth profiles of hydrogen in the thin and thick GeO_2 films with (w/) and without (w/o) 400 °C vacuum annealing. Regardless of the film thickness, the vacuum annealing at 400 °C reduces the hydrogen concentration in GeO_2, which is clearly related to the electrical improvement of Ge-MOS as described in Ref. 8. Moreover, it is noted that the hydrogen distributions show similar slopes near the interface in both the thin and thick GeO_2 layers. This result clearly suggests that the hydrogen distribution near the interface is determined by the distance from the interface, independent of the distance from the surface. A schematic illustration of the hydrogen distribution in GeO_2 on the basis of our study is shown in Fig. 5(b). The diffusion distribution of hydrogen in GeO_2 originated from two unusual diffusion processes at the surface and interface of the GeO_2/Ge. One, depending on the distance from the surface, is subject to the diffusion process in GeO_2 from air (diffusion limiting process). It is an inevitable phenomenon accompanied by a serious structural change if GeO_2, which has a characteristic of moisture absorption, was exposed to air. The other depends on the distance from the GeO_2/Ge interface. Kita *et al.* reported that GeO volatilization, is generated at the GeO_2/Ge interface and the volatilization rate is subject to the GeO diffusion process in the GeO_2 film.[14] The hydrogen distribution near the interface seems to indicate the amount of reactive sites related to oxygen vacancies, which
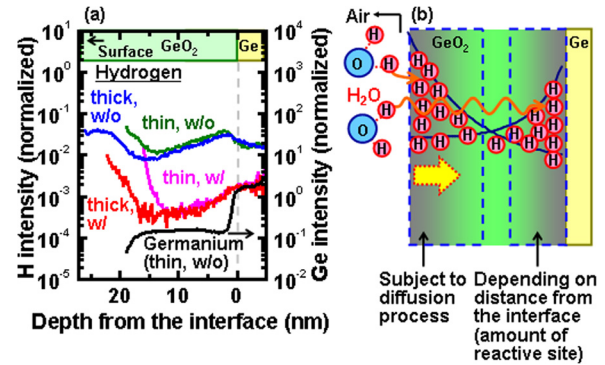

FIG. 5. (Color online) (a) SIMS depth profiles of hydrogen in thin and thick GeO_2 films. The samples without (w/o) and with (w/) 400 °C vacuum annealing are shown, respectively. The samples after the vacuum annealing were stored in analytical chambers with no air exposure by means of the transferring in an inert gas. Spectrum calibration is the same as that in Fig. 3. (b) Schematic illustration of hydrogen distribution in GeO_2. The hydrogen distribution in GeO_2 is restricted by two independent processes, which lead to different behaviors at surface and interface of GeO_2/Ge.

are caused by the GeO volatilization at the GeO_2/Ge interface. Assuming that these vacancy sites capture mobile hydrogen related species with a high diffusion coefficient, we can explain this unusual impurity absorption by GeO_2. However, further investigation is required to determine the physical origin of the diffusing species and their trap sites.

In summary, we have investigated the physical properties of GeO_2, which seem to strongly affect the electrical properties of a Ge-MOS, using various physical analyses. The unusual moisture absorbability of GeO_2 gives rise to structural deterioration and absorption of some organic molecules. We have also clarified that the hydrogen distribution in GeO_2 originated from two unusual diffusion processes at the surface and at the interface of GeO_2/Ge. We suggest that understanding the complicated behavior and controlling the physical properties of the GeO_2/Ge stacks will lead to establishing innovative Ge-MOS technologies.

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