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Insight into unusual impurity absorbability of GeO_2 in GeO_2/Ge stacks

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Shingo Ogawa, Taichi Suda, Takashi Yamamoto, et al.



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Insight into unusual impurity absorbability of GeO₂ in GeO₂/Ge stacks

Shingo Ogawa,^{1,a)} Taichi Suda,¹ Takashi Yamamoto,^{1,2} Katsuhiro Kutsuki,² Iori Hideshima,² Takuji Hosoi,^{2,b)} Takayoshi Shimura,² and Heiji Watanabe²

¹Toray Research Center, Inc., 3-3-7 Sonoyama, Otsu, Shiga 520-8567, Japan

²Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan

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Adsorbed species and its diffusion behaviors in GeO₂/Ge stacks, which are future alternative metal-oxide-semiconductor (MOS) materials, have been investigated using various physical analyses. We clarified that GeO₂ rapidly absorbs moisture in air just after its exposure. After the absorbed moisture in GeO₂ reaches a certain limit, the GeO₂ starts to absorb some organic molecules, which is accompanied by a structural change in GeO₂ to form a partial carbonate or hydroxide. We also found that the hydrogen distribution in GeO₂ shows intrinsic characteristics, indicative of different diffusion behaviors at the surface and at the GeO₂/Ge interface. Because the impurity absorbability of GeO₂ has a great influence on the electrical properties in Ge-MOS devices, these results provide valuable information in realizing high quality GeO₂/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 GeO₂, which is a fundamental dielectric for Ge-MOS just like SiO₂ 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 GeO₂/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 GeO₂/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 Al₂O₃ layer capped on the GeO₂ surface.⁸ Meanwhile, Kutsuki *et al.* reported that surface nitridation on ultrathin GeO₂ was an effective way to improve the electrical properties (drastic suppression of leakage current, etc.) compared to the GeO₂/Ge stacks,⁹ inferring that the nitride (Ge₃N₄) film on GeO₂ works as a barrier layer against the chemical reaction of GeO₂ with air. These studies might indicate that the impurity absorbability of GeO₂ 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 GeO₂/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 GeO₂, 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. GeO₂ dielectric films (20–30 nm) were fabricated by dry oxidation at 550 °C for 4–6 h using a conventional furnace. The GeO₂/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 GeO₂ as a reference and compared its physical property with that of GeO₂ after air exposure for 7 days. The adsorbed species in the GeO₂ were characterized by Fourier transform infrared spectroscopy (FT-IR). The amount of absorbed moisture in the GeO₂, when exposed to air for 7 days, was quantified by temperature programmed desorption mass spectrometry (TPD-MS). The adsorbed organic molecules on the GeO₂ and depth profiles of the impurities in the GeO₂ 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 GeO₂ focusing on the reaction between the GeO₂ and moisture (H₂O) in the air, the annealed samples at 300 °C for 30 min under vacuum were exposed to saturated D₂O (heavy water) moisture in an N₂ 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 D₂O instead of H₂O was to distinguish the hydrogen (deuterium) of the moisture from that of organic contamination. The depth profiles of the deuterium in the GeO₂ for different D₂O moisture exposure times were obtained by dynamic SIMS.

^{a)}Electronic mail: Shingo_Ogawa@trc.toray.co.jp.

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

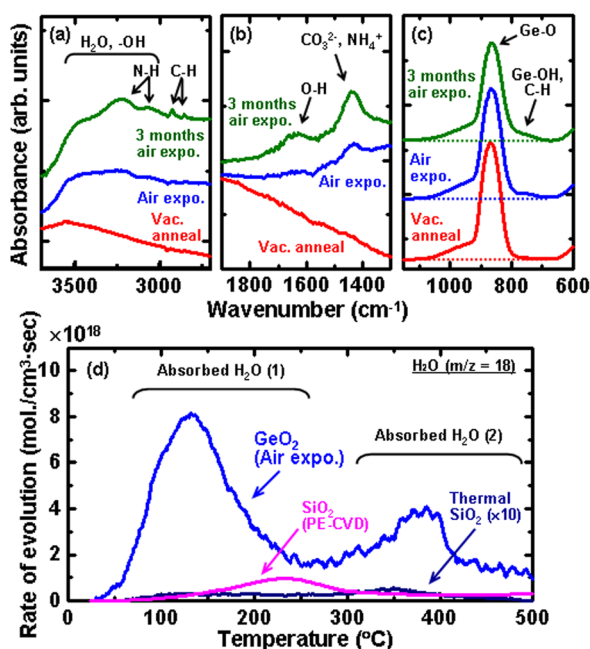


FIG. 1. (Color online) (a)–(c) FT-IR absorption spectra of GeO₂ after air exposure for 3 months (3 months air expo.), after air exposure for 7 days (air expo.), and after 300 °C vacuum annealing (vac. anneal). (d) Moisture desorption curves of GeO₂ (air expo.) and SiO₂ (PE-CVD and thermally grown; see Ref. 12) obtained from TPD-MS. Absorbed H₂O (2) is assigned to confined H₂O in GeO₂.

Figures 1(a)–1(c) show the FT-IR absorption spectra of GeO₂ 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 GeO₂ 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 GeO₂ 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 GeO₂ unlike SiO₂. Fig. 1(d) shows the moisture desorption curve of GeO₂ after air exposure for 7 days and that of SiO₂ (Ref. 11) formed by two different processes [plasma enhanced chemical vapor deposition (PE-CVD) and thermally grown]. The amount of moisture absorption by GeO₂ was around one order of magnitude higher than that by SiO₂. These results revealed that GeO₂ 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 GeO₂ after air exposure for 7 days and GeO₂ after 300 °C vacuum annealing. In order to compare GeO₂ with SiO₂, the results of the native SiO₂ (Ref. 12) [SiO₂ (air expo.)] are also shown in Fig. 2. The TOF-SIMS results show that no specific molecules exist on the GeO₂ compared to SiO₂. On the other hand, some molecules (¹⁸NH₄⁺, etc.) on GeO₂ after 300 °C vacuum annealing were lower than that on GeO₂ after air exposure for 7 days.

To investigate the depth profiles of impurities (hydrogen, carbon, and nitrogen) in GeO₂, dynamic SIMS analyses were

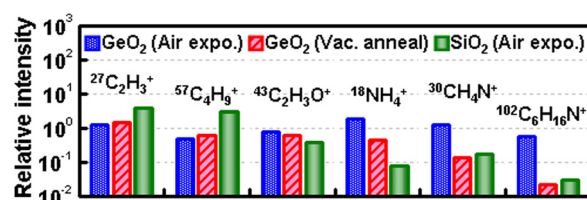


FIG. 2. (Color online) Relative intensities of various secondary ion peaks in TOF-SIMS spectra of GeO₂ after air exposure for 7 days (air expo.), after 300 °C vacuum annealing (vac. anneal), and native SiO₂ [SiO₂ (air expo.); see Ref. 14]. Intensities of the ion peaks of GeO₂ and SiO₂ are normalized by ⁷⁴Ge⁺ and ³⁰Si⁺, respectively.

carried out for GeO₂ after air exposure for 7 days and GeO₂ after 300 °C vacuum annealing, as shown in Figure 3. The concentration of each impurity in GeO₂ after 300 °C vacuum annealing was lower than that in GeO₂ after air exposure for 7 days. Although carbon and nitrogen were distributed near the surface of the GeO₂, hydrogen was distributed throughout the GeO₂ layer. Moreover, the hydrogen concentration in GeO₂ gradually increased toward the GeO₂/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 GeO₂ under a humid atmosphere. Figures 4(a) and 4(b) show SIMS depth profiles of deuterium and carbon for different D₂O moisture exposure times (0.1, 1, 10, and 60 min). It is noted that the reaction between the moisture and GeO₂ was intentionally accelerated by exposing GeO₂ to a high humidity D₂O atmosphere (80-90%). Fig. 4(a) revealed that deuterium rapidly diffuses into the GeO₂ just after the D₂O exposure, and the deuterium concentration increased with the D₂O exposure time. On the other hand, carbon does not diffuse into GeO₂ for at least 10 min, but the carbon concentration in GeO₂ drastically increased after a 60-min exposure. Fig. 4(c) shows the D₂O exposure time versus the deuterium, carbon, and germanium intensity at a 10-nm depth. Because the deuterium concentration in GeO₂ is proportional to the square root of time, the distribution of deuterium, representing hydrogen derived from moisture, is subject to a diffusion process in GeO₂ from the air, which has a diffusion coefficient according to Fick's second law.¹³

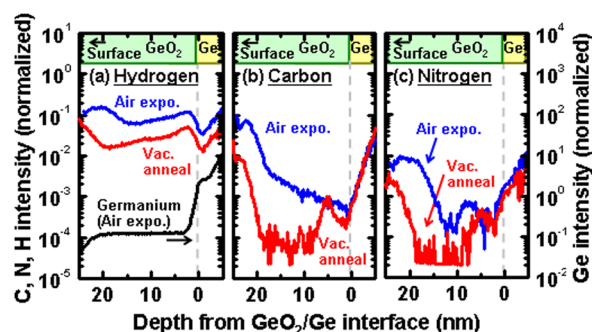


FIG. 3. (Color online) SIMS depth profiles of (a) hydrogen, (b) carbon, and (c) nitrogen in GeO₂ after air exposure for 7 days (air expo.) and after 300 °C vacuum annealing (vac. anneal). Horizontal axis (depth) was shown on the basis of GeO₂/Ge interface determined from Ge profile in Fig. 3(a) and vertical 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.

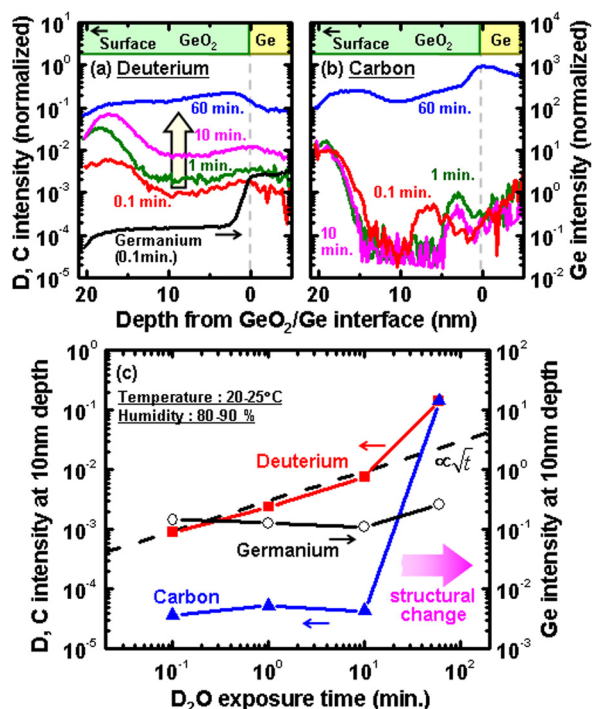


FIG. 4. (Color online) SIMS depth profiles of (a) deuterium and (b) carbon in GeO₂ films for different D₂O moisture exposure times of 0.1, 1, 10, and 60 min. Spectrum calibration is the same as that in Fig. 3. (c) Intensities of deuterium, carbon, and germanium at 10-nm depth depending on the D₂O exposure time.

After the D₂O exposure for 60 min, the deuterium, carbon and germanium drastically increased. These results revealed that when the hydrogen concentration in GeO₂ has reached a certain limit, GeO₂ starts to absorb a lot of impurities (carbon, etc.) along with some structural changes.

Finally, the diffusion distribution of hydrogen in GeO₂ was measured in detail. Figure 5(a) shows the depth profiles of hydrogen in the thin and thick GeO₂ 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 GeO₂, 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 GeO₂ 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 GeO₂ on the basis of our study is shown in Fig. 5(b). The diffusion distribution of hydrogen in GeO₂ originated from two unusual diffusion processes at the surface and interface of the GeO₂/Ge. One, depending on the distance from the surface, is subject to the diffusion process in GeO₂ from air (diffusion limiting process). It is an inevitable phenomenon accompanied by a serious structural change if GeO₂, which has a characteristic of moisture absorption, was exposed to air. The other depends on the distance from the GeO₂/Ge interface. Kita *et al.* reported that GeO volatilization, is generated at the GeO₂/Ge interface and the volatilization rate is subject to the GeO diffusion process in the GeO₂ film.¹⁴ The hydrogen distribution near the interface seems to indicate the amount of reactive sites related to oxygen vacancies, which

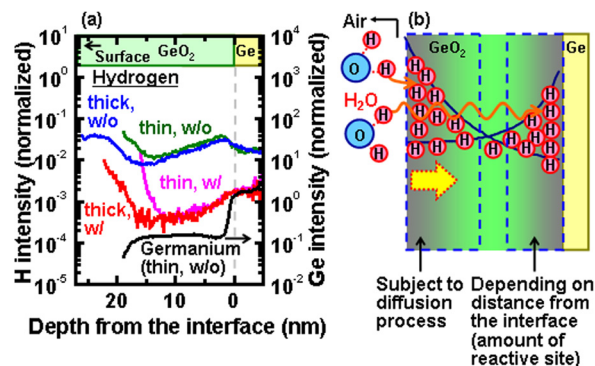


FIG. 5. (Color online) (a) SIMS depth profiles of hydrogen in thin and thick GeO₂ films. The samples without (w/o) and with (w/) 400 °C vacuum annealing were shown, respectively. The samples after the vacuum annealing were stored in analytical chambers with no air exposure by means of the transferring in an inert gas. Spectrum calibration is the same as that in Fig. 3. (b) Schematic illustration of hydrogen distribution in GeO₂. The hydrogen distribution in GeO₂ is restricted by two independent processes, which lead to different behaviors at surface and interface of GeO₂/Ge.

are caused by the GeO volatilization at the GeO₂/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 GeO₂. 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 GeO₂, which seem to strongly affect the electrical properties of a Ge-MOS, using various physical analyses. The unusual moisture absorbability of GeO₂ gives rise to structural deterioration and absorption of some organic molecules. We have also clarified that the hydrogen distribution in GeO₂ originated from two unusual diffusion processes at the surface and at the interface of GeO₂/Ge. We suggest that understanding the complicated behavior and controlling the physical properties of the GeO₂/Ge stacks will lead to establishing innovative Ge-MOS technologies.

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