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Origin of flatband voltage shift and unusual minority carrier generation in thermally grown GeO_2/Ge metal-oxide-semiconductor devices

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Improvement in electrical properties of thermally grown GeO_2/Ge metal-oxide-semiconductor (MOS) capacitors, such as significantly reduced flatband voltage (V_{FB}) shift, small hysteresis, and minimized minority carrier response in capacitance-voltage (*C-V*) characteristics, has been demonstrated by *in situ* low temperature vacuum annealing prior to gate electrode deposition. Thermal desorption analysis has revealed that not only water but also hydrocarbons are easily infiltrated into GeO_2 layers during air exposure and desorbed at around 300 °C, indicating that organic molecules within GeO_2/Ge MOS structures are possible origins of electrical defects. The inversion capacitance, indicative of minority carrier generation, increases with air exposure time for Au/GeO_2/Ge MOS capacitors, while maintaining an interface state density (D_{it}) of about a few 10^{11} cm^{-2} eV^{-1}. Unusual increase in inversion capacitance was found to be suppressed by Al_2O_3 capping (Au/Al_2O_3/GeO_2/Ge structures). This suggests that electrical defects induced outside the Au electrode by infiltrated molecules may enhance the minority carrier generation, and thus acting as a minority carrier source just like MOS field-effect transistors. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3143627]

Germanium is an attractive channel material for future metal-oxide-semiconductor (MOS) field-effect transistors because it has higher carrier mobility than conventional silicon. However, compared with silicon oxide gate insulator, germanium oxide is difficult to integrate into a MOS fabrication process due to its poor thermal stability and water solubility. Thermal decomposition of GeO_2 is caused by GeO molecule desorption by annealing at above 425 °C.[1] It has been pointed out that abstracting Ge from a Ge substrate at a GeO_2/Ge interface is essential for GeO molecule formation, and this interface reaction leads to GeO_2/Ge interface property seriously deteriorating.[2] This thermal instability is one reason D_{it} values of thermally grown GeO_2/Ge interface reported to date are scattered widely (10^{11}–10^{12} cm^{-2} eV^{-1}). Meanwhile, it has recently been reported that a GeO_2 insulator formed by high pressure thermal oxidation at 550 °C, which can suppress the GeO volatilization, exhibits improved electrical properties.[3] Matsubara *et al.*[4] also demonstrated that D_{it} values of less than 10^{11} cm^{-2} eV^{-1} were obtained for GeO_2/Ge interfaces formed by a standard dry oxidation at about 550–575 °C. A good interface property of as-oxidized GeO_2/Ge(100) interface at above 500 °C was predicted from a simple calculation on the basis of viscoelastic properties of GeO_2.[5] Our first-principles total energy calculation of the GeO_2/Ge interface during thermal oxidation also suggests a superior interface property because of a low Ge emission probability at the interface during oxidation.[6] However, experimental verification of these predictions on the standard thermal GeO_2/Ge interface is demonstrated in only a few reports.[4,7,8] This may be attributed to the fact that Ge MOS characteristics are highly sensitive to fabrication process conditions due to hygroscopic and volatile properties of GeO_2. In addition, since the minority carrier response is more pronounced in Ge MOS capacitors, the difficulty in obtaining accurate D_{it} values using a conventional conductance method has been pointed out.[9–12] Thus, to minimize the minority carrier generation, low temperature measurements are widely used.

Remarkable inversion capacitance in Ge MOS capacitors is generally considered to originate from a much shorter minority carrier response time and higher minority carrier generation-recombination rate, due to the smaller band gap of Ge. However, in many previous reports on Ge MOS devices, frequency dispersion of *C-V* curves in the inversion region is not unique and seems to depend on process conditions. This fact suggests that the minority carrier generation is caused not only by intrinsic thermal excitation across the Ge band gap but also by another excitation process, such as defect-assisted band tunneling. Furthermore, although a negative V_{FB} shift is often observed for Ge MOS capacitors, its origin has not yet been addressed. In this study, we have systematically investigated the correlation between electrical characteristics of Ge MOS devices and hygroscopic property of GeO_2. The impact of *in situ* low-temperature vacuum annealing prior to gate electrode deposition on Ge MOS characteristics was examined in terms of V_{FB} shift, *C-V* hysteresis, and interface quality. We also discuss a minority carrier generation mechanism on the basis of time evolution of *C-V* characteristics of Ge MOS capacitors with/without Al_2O_3 capping on GeO_2 insulators (Au/GeO_2/Ge or Au/Al_2O_3/GeO_2/Ge) during air exposure.

The starting substrates were *p*-type Ge(100) wafers with a resistivity of 0.1–0.5 Ω cm. The substrates were cleaned using cyclic 10% HF dip and ultrapure water rinse. After

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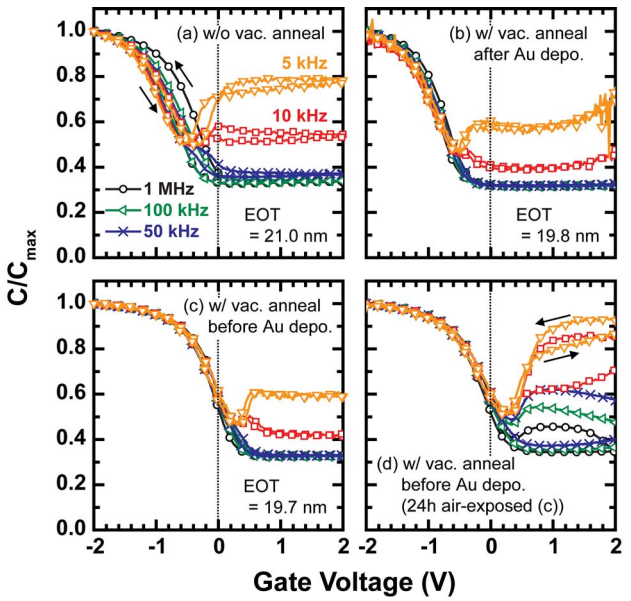

FIG. 1. (Color online) Bidirectional normalized *C-V* curves of the as-fabricated $Au/GeO_2/Ge$ MOS capacitors (a) without vacuum annealing but with *in situ* vacuum annealing (b) after and (c) before Au deposition. (d) *C-V* curves of the $Au/GeO_2/Ge$ MOS capacitor with *in situ* vacuum annealing prior to the Au deposition measured after air exposure for 24 h.

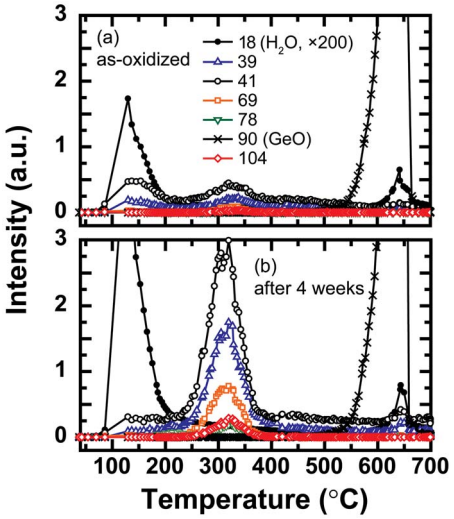

FIG. 2. (Color online) Thermal desorption spectra taken from (a) an as-oxidized sample and (b) a sample exposed to air for 4 weeks after oxidation.

blow-drying, the samples were loaded into a furnace tube and subjected to dry oxidation in an O_2 ambient at 550 °C for 2 h to form a GeO_2 layer. Then the samples were immediately transferred from the furnace to a vacuum evaporation chamber in order to minimize water absorption from the air. Au films were deposited through a shadow mask to define gate electrodes at room temperature. Some of the samples were *in situ* annealed at 300 °C for 30 min under a vacuum of 6×10^{-4} Pa either before or after Au deposition. Al backside electrodes were also formed by the vacuum evaporation. The *C-V* characteristics were measured from inversion to accumulation at frequencies ranging from 1 kHz to 1 MHz using an Agilent 4284 LCR meter. An equivalent oxide thickness, V_{FB}, and hysteresis were estimated from high frequency *C-V* curves, and D_{it} values were extracted by a low-temperature conductance method.

Figure 1 shows the bidirectional *C-V* curves of the $Au/GeO_2/Ge$ MOS capacitors fabricated under various conditions. The extracted values of V_{FB} and hysteresis are listed in Table I. Considering a Fermi level of Ge substrates and Au work function of 5.0 eV, the ideal V_{FB} of the $Au/GeO_2/Ge$ MOS capacitor is estimated to be about 0.5 V. A negative V_{FB} shift, large *C-V* hysteresis, and remarkable inversion capacitance depending on the measured frequency were observed for the capacitor without vacuum annealing [Fig. 1(a)]. An *in situ* vacuum annealing after Au deposition effectively improved *C-V* hysteresis and suppressed minority carrier response but had almost no effect on V_{FB} [Fig. 1(b)]. In addition to these improvements, the negative V_{FB} shift was significantly reduced by *in situ* vacuum annealing prior to Au deposition [Fig. 1(c)]. However, the frequency dispersion of *C-V* curves in the inversion region arose again after air exposure for 24 h, while maintaining small V_{FB} shift and hysteresis [Fig. 1(d)]. These results indicate that hygroscopic property of GeO_2 strongly affects the electrical characteristics of Ge MOS capacitors. Since the *C-V* hysteresis was reduced by vacuum annealing regardless of an existing Au electrode, carrier trapping sites in GeO_2 are considered to have been decreased due to temperature-induced structural change [see Figs. 1(b) and 1(c)]. The V_{FB} closer to the ideal value was obtained only by *in situ* vacuum annealing prior to Au deposition and was stable when exposed to air [see Figs. 1(c) and 1(d)]. Furthermore, we found that when it took a few hours after oxidation to introduce a sample into the vacuum evaporation chamber, the resulting *C-V* curve shifted much more negatively. These results suggest that infiltrated molecules into GeO_2 layer are a possible origin of the negative V_{FB} shifts, such as fixed sheet charge generation, and can be removed by low temperature vacuum annealing.

TABLE I. Extracted values of V_{FB} and hysteresis from the *C-V* curves measured at 1 MHz of the fabricated $Au/GeO_2/Ge$ MOS capacitors shown in Fig. 1.

	Sample	V_{FB} (V)	Hysteresis (mV)
(a)	without vac. anneal	−0.76	320
(b)	with vac. anneal after Au depo.	−0.90	114
(c)	with vac. anneal before Au depo.	−0.14	88
(d)	with vac. anneal before Au depo. (after air exposure for 24 h)	−0.20	90

To characterize the infiltrated molecules, thermal desorption spectroscopy (TDS) analyses were carried out for both an as-oxidized sample and a sample exposed to air for 4 weeks after oxidation, as shown in Fig. 2. It was found that the several mass numbers, such as 39, 41, 69, 78, and 104, were detected at around 300 °C and that the amount of those molecules significantly increased as the time passed after oxidation (air exposure time). Although it was difficult to identify these peaks as specific molecules only from TDS spectra, recent infrared absorption spectroscopy analysis on Ge(100) surfaces revealed that a large amount of hydrocarbons (CH_x) were incorporated by air exposure with a growth of native oxide.[13] Therefore, we think that several molecules desorbed at low temperatures were attributable to organic molecules in GeO_2.

Next, we examined time evolution of the *C-V* characteristics during air exposure. It was found that although minor-

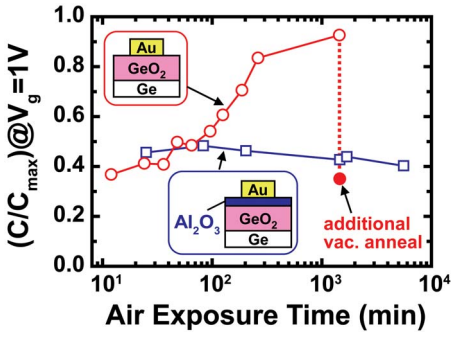

FIG. 3. (Color online) Time evolution of normalized inversion capacitance at the gate voltage of 1 V taken from the forward *C-V* curves measured at 10 kHz for both Au/GeO_2/Ge and Au/Al_2O_3/GeO_2/Ge MOS capacitors.

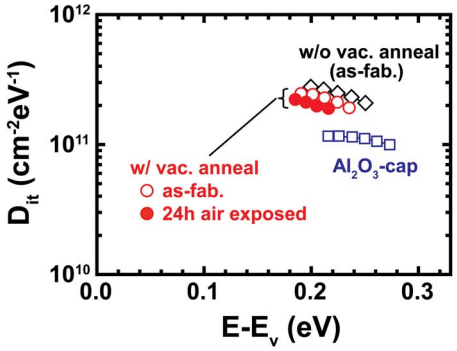

FIG. 4. (Color online) Energy distribution of D_{it} for GeO_2/Ge interfaces *in situ* vacuum annealed prior to Au electrode deposition, subsequent air exposure for 24 h, and Al_2O_3 capping layer formation, measured by low temperature conductance method.

ity carrier response was suppressed by *in situ* vacuum annealing both with and without an Au electrode, it became more and more pronounced during air exposure, as indicated by red open circles in Fig. 3. In contrast, the values of V_{FB} and *C-V* hysteresis did not show any notable change even after air exposure for 24 h, as shown in Fig. 1(d). This indicates that while an Au electrode blocks the organic molecules from diffusing into the bottom GeO_2 layer, the outer region exposed to the air deteriorates. The remarkable increase in inversion capacitance due to air exposure was drastically reduced again by additional vacuum annealing, as indicated by the red filled circle in Fig. 3. This situation is quite similar to *in situ* vacuum annealing after Au deposition [Fig. 1(b)]. Furthermore, to completely exclude any influence from air exposure, we fabricated the Au/Al_2O_3/GeO_2/Ge MOS capacitor. Right after the vacuum annealing, an Al_2O_3 capping layer was formed on GeO_2 by oxidizing a thin metal Al layer at 400 °C under low oxygen partial pressure conditions. As shown in Fig. 3, the Au/Al_2O_3/GeO_2/Ge MOS capacitor exhibited a stable inversion capacitance against air exposure. From these results, it can be concluded that the infiltrated molecules into GeO_2 layer in the uncovered region induces electrical defects, thus enhancing minority carrier generation. One of the possible mechanisms is that the electrical defects near GeO_2/Ge interface caused by infiltrated molecules assisted the valence electron tunneling in the Ge substrate, hence generated electrons were supplied to a depletion layer just beneath the Au electrode under inversion conditions, just like MOS field-effect transistors.

Finally, the impact of *in situ* vacuum annealing, air exposure, and Al_2O_3 capping layer formation on GeO_2/Ge interface properties was also evaluated. As shown in Fig. 4, there was almost no difference in D_{it} values (2×10^{11} cm^{-2} eV^{-1}) between with and without *in situ* vacuum annealing, implying that the GeO_2/Ge interface was not deteriorated by air exposure for a short time. The D_{it} values remained unchanged even after air exposure for 24 h because the Au electrode just above the measured region of the GeO_2/Ge interface blocked the molecules. The Au/Al_2O_3/GeO_2/Ge MOS capacitor exhibited slightly lower D_{it}, but further investigation is required to conclude whether Al_2O_3 capping improves the GeO_2/Ge interface quality or not. Among these measurements, low D_{it} values were obtained for GeO_2/Ge interface, which were comparable to the reported values.[4,7] This indicates the inherently superior interface quality of GeO_2/Ge interface without any interface passivation technique.

In summary, we have demonstrated a significant improvement in electrical properties of GeO_2/Ge MOS capacitors, such as a reduced flatband voltage shift, small *C-V* hysteresis, suppression of minority carrier response, and low D_{it} of about a few 10^{11} cm^{-2} eV^{-1}, by *in situ* low temperature vacuum annealing prior to gate electrode deposition. We also found that organic molecules infiltrating into GeO_2 layers during air exposure strongly affects the V_{FB} and minority carrier generation. These results provide a useful processing guideline for achieving Ge MOS technologies.

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