Improvement in *C-V* characteristics of Ge metal-oxide semiconductor capacitor by H_2O_2 incorporated HCl pretreatment

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Electrical characteristics of high-κ/Ge metal-oxide semiconductor (MOS) capacitors pretreated with HCl or HF solutions are investigated, including the effect of H_2O_2 incorporation. HCl treatment is more effective than HF treatment for decreasing equivalent oxide thickness. H_2O_2 incorporation into HCl solution leads to dramatic decrease in the capacitance at inversion side. We have confirmed that residual metal impurities are reduced below 10^{10} atoms/cm^2 on the Ge surface after pretreatment with mixed solution of HCl and H_2O_2. We conclude that decrease in metal impurities at Ge surface is responsible for the superior *C-V* characteristic of Ge MOS capacitor. [DOI: 10.1063/1.2857477]

Ge is one of the most attractive channel materials for post-Si technology because high-κ/Ge gate stacks have the potential to offer high channel mobility and thin equivalent oxide thickness (EOT) simultaneously.[1] In particular, *p*-channel Ge field-effect transistor (FET) is promising since bulk hole mobility of Ge is four times that of Si.[2] Although superior properties of GeO_2/Ge interface just after formation have been reported, since a dielectric constant of GeO_2 is low (~7) (Ref. 3) and GeO_2/Ge gate stack not only decomposes into GeO(solid) (Refs. 4 and 5) but also desorbs as GeO(gas) (Refs. 5 and 6) at a temperature around 400 °C that is the lower limit to activate source/drain dopant,[1,7] it is better to remove Ge oxide from Ge surface when fabricating Ge metal-oxide semiconductor (MOS)-FETs. In order to reduce Ge oxide thickness, it is essential to select appropriate pretreatment for Ge surface prior to high-κ film deposition. The results of applying surface analysis techniques indicate that halogen acid wet solutions excluding HF are effective for suppressing the formation of Ge oxide,[8–10] in which case influences of the pretreatment on electrical characteristics of the MOS capacitor are still limited.[11] In this paper, the effects of HCl pretreatment for Ge surface prior to high-κ film deposition on electrical characteristics and physical properties are systematically investigated.

Sb lightly doped *n*-type Ge substrate (~1 Ω cm) is treated with 20% HF or 20% HCl. In addition to HF treatment (treatment A) and HCl treatment (treatment B), sequential wet processes with HCl and 35% H_2O_2 (treatment C), and HCl treatment with 0.1% H_2O_2 (treatment D) are also practiced. All these pretreatments are cyclically repeated and followed by de-ionized water rinse. Zr silicate (ZrSiO, Zr:Si=1:1) layer of 5 nm thickness and TiN layer of 50 nm thickness are deposited by sputtering as a high-κ gate insulator and a gate electrode, respectively. The gate electrode (100×100 μm^2) is defined by resist lift-off process. MOS capacitors are annealed at 400 °C in N_2 gas for 30 min followed by 350 °C forming gas annealing for 30 min. X-ray photoelectron spectroscopy (XPS) after the pretreatments is performed using monochromatic Al $K\alpha$ x-ray source (1486.6 eV) and corrected using the C 1*s* peak position (284.8 eV). The take-off angle of photoelectron in this measurement is 15°. The thickness of the surface oxide after the pretreatments is evaluated from the XPS peak intensity ratio of Ge oxide to Ge substrate[12] by using inelastic mean free path of 2.88 nm calculated by TPP-2M equation,[13] assuming that density of Ge oxide is the same as that of hexagonal GeO_2 of 4.23 g/cm^3, bandgap of Ge oxide is 3.98 eV,[14] and molecular weight of Ge oxide is the average of that of Ge monoxide (GeO) and that of Ge dioxide (GeO_2). High-resolution cross-sectional transmission electron microscopy (TEM) is employed to investigate the interface at high-κ/Ge gate stacks. *C-V* measurements are performed at around −50 °C in order to prevent minority carrier response depending on intrinsic carrier density (n_i).[15,16] The value of n_i decreases from 2×10^{13} to 7×10^{10} cm^{-3} by changing measurement temperature from 20 to −50 °C. Measurement frequency of 1 kHz is chosen to emphasize the difference of the capacitance at inversion side in the samples with different pretreatments, whereas that of 100 kHz is used to deduce an activation energy (E_{act}) to generate minority carrier at the inversion side from Arrhenius plot of the inversion conductance (G_I) (Refs. 15 and 16) evaluated at V_g of −2 V at the measurement temperateure around −50 °C. Inductively coupled plasma mass spectrometry (ICP-MS) is used to detect residual metal impurity on Ge surface.

XPS Ge 3*d* spectra obtained from Ge surfaces just after cleaning with treatment B and D are shown in Fig. 1. Small peaks of Ge oxides that consist of GeO (Ge^{2+}) and GeO_2 (Ge^{4+}) are seen in both specimens beside strong peaks of Ge substrate. The thin oxide thickness of 0.42 nm for the sample with treatment D is slightly thicker than that of 0.36 nm for the sample with the treatment B, indicating that H_2O_2 oxidizes suboxide or Ge substrate. A slightly large chemical shift of the oxide peak toward large oxidation state is the other evidence for the H_2O_2 oxidation. Since GeO_2 is soluble in water,[17] most of the GeO_2 is removed at the pretreatment, resulting in little difference in the oxide thickness irrespective of H_2O_2 incorporation in HCl solution.

Figures 2(a) and 2(b) show very smooth interface between ZrSiO and Ge irrespective of H_2O_2 incorporation in HCl solution, although it is reported that surface roughness increases after H_2O_2 treatment.[18] Chemically stable Ge oxide

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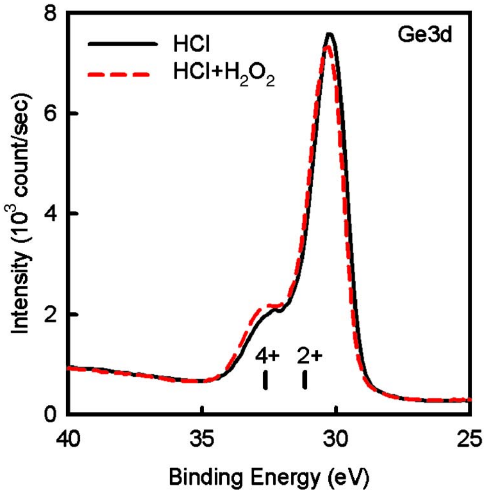

FIG. 1. (Color online) XPS Ge 3*d* spectra of Ge surface pretreated by HCl and by HCl with H_2O_2. Reported chemical shift positions of Ge^{4+} and Ge^{2+} are also shown (Ref. 4).

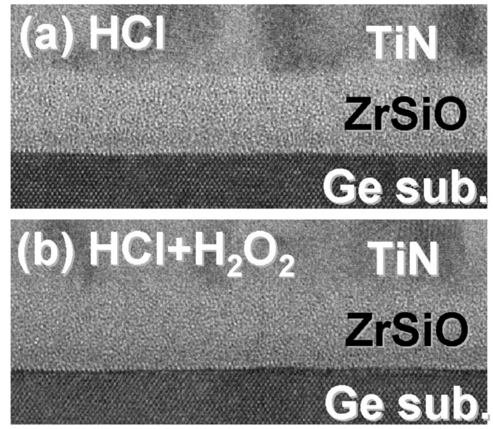

FIG. 2. Cross-sectional TEM images of TiN/ZrSiO/Ge MOS capacitor pretreated by (a) HCl and (b) HCl with H_2O_2 and annealed at 400 °C in N_2 and at 350 °C in forming gas.

layer, Cl-terminated Ge surface,[9,19] or low H_2O_2 concentration of 0.1%, which prevents the oxidation of Ge surface with H_2O_2, may be responsible for the smooth interface. The suppression of Ge surface oxidation means that H_2O_2 oxidizes Ge suboxide as indicated by the XPS results reported above.

C-V curves of TiN/ZrSiO/*n*-Ge MOS capacitors with different pretreatments are shown in Fig. 3. Accumulation capacitances (C_{acc}) of the capacitors pretreated by HCl-related solutions (treatments B, C, and D) are larger than that of the capacitor pretreated with HF (treatment A). The increase in C_{acc} in the HCl-treated samples reflects the decrease in the residual Ge oxide thickness expected from the previously reported physical analyses.[8–10] On the other hand, a severe increase in the capacitance at the inversion side (ΔC_{inv}), which comes from minority carrier response, is clearly seen in the case of treatments A and B. H_2O_2 incorporation into the pretreatment is effective for decreasing ΔC_{inv} (treatments C and D). In general, there are several different mechanisms to generate minority carrier at the inversion side such as generation-recombination processes through semiconductor midgap traps ($E_{act} \sim E_g/2$), diffusion from the bulk neutral region to the interface ($E_{act} \sim E_g$), and/or the existence of an inversion layer.[15,16] Since E_{act} of treatments B, C, and D are 0.29, 0.21, and 0.22, respectively, ΔC_{inv} mainly comes from the generation of electron-hole pairs through bulk traps in the depletion layer. It is noted that minority carrier response by bulk traps with midgap energy level in Ge substrate can be also easily judged from the constant shape of the capacitance and the conductance of *C-V* curves irrespective of V_g at inversion side.[15]

In order to determine the origin of the ΔC_{inv} improvement depending on the pretreatment, we analyzed residual amounts of Cu and Fe on Ge surface after each HCl-related pretreatment by ICP-MS. Cu and Fe are known to have the impurity levels near midgap in Ge[2], meaning these atoms can act as the bulk traps. As shown in Fig. 4, large amounts of Cu and Fe, over 10^{11} atoms/cm^2, are observed for the Ge wafer before pretreatment, meaning that initial Ge oxide is contaminated with these metals. The amounts of metals on Ge surfaces are decreased with treatment B and further decreased with treatment C. And finally, metal impurities at the surface are reduced below the detection limit (DL) of ICP-MS analysis for Cu of 5×10^9 atoms/cm^2 and Fe of 6×10^9 atoms/cm^2 in the case of the specimen with treatment D. Therefore, we conclude that the removal of metal-contaminated initial Ge oxide causing metal diffusion and deep-level formation in Ge substrate during the thermal process are responsible for the improved ΔC_{inv}. Effective removal of metal atoms from the Ge surface is considered to be a result of removal of GeO_2 by once oxidizing GeO layer contaminated with metals into GeO_2 and then dissolving

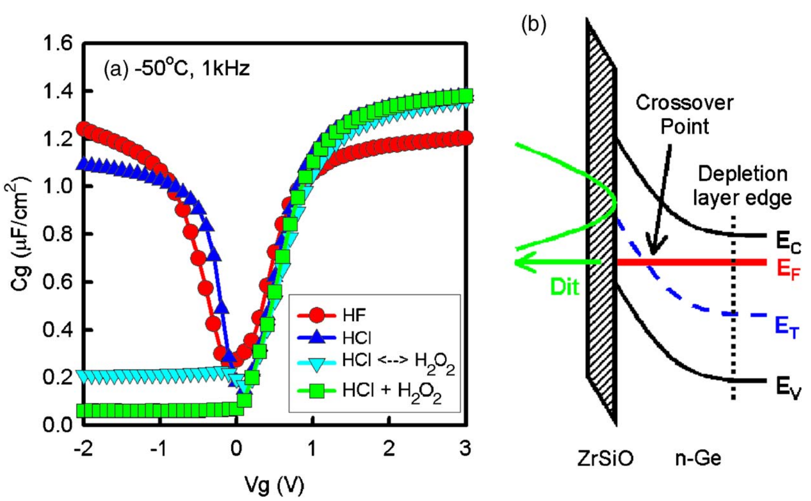

FIG. 3. (Color online) (a) *C-V* characteristics measured from TiN/ZrSiO/*n*-Ge capacitors pretreated with halogen acid. (b) Schematic energy-band diagram of Ge MOS capacitor to explain ΔC_{inv} at the inversion side in (a) due to bulk trap in Ge substrate where E_T denotes trap energy level of bulk trap in Ge.

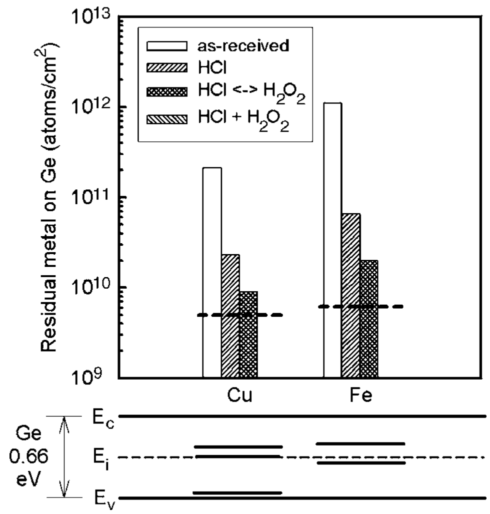

FIG. 4. Residual Cu and Fe on Ge surface after pretreatments measured by ICP-MS. Data for as-received Ge wafer are also shown for reference. Dashed lines denote detection limit (DL) for Cu and Fe in ICP-MS, respectively. Residual Cu and Fe decrease below DL after HCl treatment with H_2O_2. Impurity levels of Cu and Fe in Ge (Ref. 2) are also shown below.

GeO_2 in water.[5] Since treatment C is clearly more effective for both electrical characteristics (Fig. 3) and physical properties (Fig. 4) than treatment B, oxidation and dissolution of Ge oxide are key processes in Ge surface pretreatment. The effect of coexistence of H_2O_2 with HCl in treatment D, which is known as SC2 in Si process, may be partly responsible for reducing metal atoms by dissolving into the solution as ions.[17,20]

In conclusion, electrical characteristics of high-κ/Ge MOS capacitors depend on the type of pretreatment for Ge surface. Compared to HF treatment, HCl treatment prior to high-κ film deposition is more effective in decreasing EOT of the MOS capacitor. H_2O_2 incorporation into HCl solution leads to dramatic decrease in the capacitance at the inversion side of *C-V* curves. Residual amounts of metal impurities acting as deep levels in Ge such as Cu and Fe are reduced to below 10^{10} atoms/cm^2 on the Ge surface after pretreatment with HCl solution incorporating H_2O_2. Removal of metal-contaminated GeO from Ge surface, which is realized with H_2O_2 incorporation into HCl pretreatment solution, is responsible for the superior *C-V* characteristic of Ge MOS capacitors. Since solubility of Ge oxide depends on the form of the oxide and insoluble GeO can be oxidized to soluble GeO_2 by H_2O_2, the pretreatment taking the solubility and the oxidation of Ge oxide into consideration is a key issue regarding fabrication of Ge MOS device with good electrical characteristics.

[1] C. O. Chui, H. Kim, D. Chi, B. B. Triplett, P. C. McIntyre, and K. C. Saraswat, Tech. Dig. - Int. Electron Devices Meet. **2002**, 437.
[2] S. M. Sze, *Physics of Semiconductor Devices*, 2nd ed. (Wiley, New York, 1981).
[3] *CRC Handbook of Chemistry and Physics*, 75th ed. (CRC, Florida, 1994).
[4] D. Schmeisser, R. D. Schnell, A. Bogen, F. J. Himpsel, D. Rieger, G. Landgren, and J. F. Morar, Surf. Sci. **172**, 455 (1986).
[5] K. Prabhakaran, F. Maeda, Y. Watanabe, and T. Ogino, Appl. Phys. Lett. **76**, 2244 (2000).
[6] Y. Kamata, Y. Kamimuta, T. Ino, and A. Nishiyama, Jpn. J. Appl. Phys., Part 1 **44**, 2323 (2005).
[7] Y. Kamata, Y. Kamimuta, T. Ino, R. Iijima, M. Koyama, and A. Nishiyama, Jpn. J. Appl. Phys., Part 1 **45**, 5651 (2006).
[8] B. Onsia, T. Conard, S. D. Gendt, M. Heyns, I. Hoflijk, P. Mertens, M. Meuris, G. Raskin, S. Sioncke, I. Teerlinck, A. Theuwis, J. V. Steenbergen, and C. Vinckier, Diffus. Defect Data, Pt. B **103-104**, 27 (2005).
[9] S. Sun, Y. Sun, Z. Liu, D.-I. Lee, S. Peterson, and P. Pianetta, Appl. Phys. Lett. **88**, 021903 (2006).
[10] Y. Moriyama, N. Hirashita, E. Toyoda, K. Usuda, S. Nakaharai, N. Sugiyama, and S. Takagi, ECS Trans. **3**, 1183 (2006).
[11] E. P. Gusev, H. Shang, M. Copel, M. Gribelyuk, C. D'Emic, P. Kozlowski, and T. Zabel, Appl. Phys. Lett. **85**, 2334 (2004).
[12] F. J. Himpsel, F. R. McFeely, A. Taleb-Ibrahimi, J. A. Yarmoff, and G. Hollinger, Phys. Rev. B **38**, 6084 (1988).
[13] S. Tanuma, C. J. Powell, and D. R. Penn, Surf. Interface Anal. **21**, 165 (1994).
[14] K. Oishi and Y. Matsuo, Thin Solid Films **274**, 133 (1996).
[15] E. H. Nicollian and J. R. Brews, *MOS Physics and Technology* (Wiley, New York, 2002).
[16] A. Dimoulas, G. Vellianitis, G. Mavrou, E. K. Evangelou, and A. Sotiropoulos, Appl. Phys. Lett. **86**, 223507 (2005).
[17] M. Pourbaix, *Atlas of Electrochemical Equilibria in Aqueous Solutions* (Pergamon, London, 1966).
[18] J. Kim, K. Saraswat, and Y. Nishi, ECS Trans. **1**, 214 (2005).
[19] Z. H. Lu, Appl. Phys. Lett. **68**, 520 (1996).
[20] H. Morinaga, M. Suyama, M. Nose, S. Verhaverbeke, and T. Ohmi, IEICE Trans. Electron. **E79-C**, 343 (1996).