Effects of postgate dielectric treatment on germanium-based metal-oxide-semiconductor device by supercritical fluid technology

Po-Tsun Liu,^{1,a)} Chen-Shuo Huang,² Yi-Ling Huang,² Jing-Ru Lin,² Szu-Lin Cheng,³ Yoshio Nishi,⁴ and S. M. Sze⁵

¹Department of Photonics and Display Institute, National Chiao Tung University, 1001 Ta-Hsueh Rd., HsinChu 30010, Taiwan

²Department of Photonics and Institute of Electro-Optical Engineering, National Chiao Tung University, HsinChu 30010, Taiwan

³Department of Materials Science and Engineering, Stanford University, Stanford, California 94305, USA

⁴Department of Electrical Engineering, Stanford University, Stanford, California 94305, USA

⁵Department of Electronic Engineering, National Chiao Tung University, HsinChu 30010, Taiwan

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Supercritical fluid (SCF) technology is employed at low temperature as a postgate dielectric treatment to improve gate SiO₂/germanium (Ge) interface in a Ge-based metal-oxide-semiconductor (Ge-MOS) device. The SCF can transport the oxidant and penetrate the gate oxide layer for the oxidation of SiO₂/Ge interface at 150 °C. A smooth interfacial GeO₂ layer between gate SiO₂ and Ge is thereby formed after SCF treatment, and the frequency dispersion of capacitance-voltage characteristics is also effectively alleviated. Furthermore, the electrical degradation of Ge-MOS after a postgate dielectric annealing at 450 °C can be restored to a extent similar to the initial state. © 2010 American Institute of Physics. [doi:10.1063/1.3365177]

Germanium (Ge) semiconductor has been considered as an alternative channel material in place of silicon (Si) for future high-performance complementary metal-oxide-semiconductor technology, because its higher carrier mobility for both electrons and holes, lower dopant thermal activation energies for shallower junction formation and compatible fabrication processes with existing silicon manufacturing infrastructure. However, the Ge-metal-oxide-semiconductor (MOS) technology still has many challenges and not been widely deployed. The most critical issue hindering the application of Ge is lack of high-quality and stable Ge insulation oxide comparable to silicon dioxide (SiO₂) for silicon.^{1,2} The poor native Ge oxide layer would be thermally decomposed at low temperature (about 420 °C) and Ge diffuses into gate dielectric layer during the thermal deposition or postdielectric annealing (PDA) processes. Sequentially, poor interface properties and high gate leakage current will be exhibited in the Ge-MOS device.^{3–7} Various pre-gate surface modification techniques, such as surface nitridation or Si passivation, have been developed to improve the quality of gate insulator/Ge interface.¹³ It was also reported that high-performance Ge MOSFET could be realized by careful control of interfacial GeO₂ formation.² In this study, a low-temperature supercritical CO₂ (SCCO₂) fluid technology is proposed as a postgate dielectric treatment at 150 °C to improve the SiO₂/Ge interface after high-temperature PDA process. The SCCO₂, which exists above its critical pressure (1170 psi) and temperature (30 °C), provides good liquidlike solvency and high gaslike diffusivity, giving it excellent transport capacity.⁸ The oxidant is also easily dissolved in SCCO₂ fluid with specific surfactants. It is thereby allowed for SCCO₂ fluid to transport the oxidant and penetrates the dielectric layer for trap passivation and interface oxidation at

low temperature.^{9–11} The SCCO₂ fluid mixed with oxidant is proposed in this work for the formation of interfacial GeO₂ layer after gate dielectric deposition to prevent interfacial decomposition from subsequent thermal processes.

A 0.5 Ω cm p-type (100) Si wafer was cleaned with standard RCA clean process and immediately loaded into the Applied Materials reduced-pressure chemical vapor deposition reactor. The initial 600 nm thick Ge film was grown at 400 °C with a GeH₄ partial pressure of 8 Pa. Annealing under H₂ ambient was then performed at 825 °C for 40 min. The growth temperature was ramped to 600 °C for the deposition of another 1.4 μm-thick Ge layer at 8 Pa, followed by a 15 min H₂ bake at 750 °C. This epitaxial Ge (epi-Ge) layer is p-type with an electrically activated concentration of 4 × 10¹⁵ cm⁻³. The wafer was immediately loaded into a low-pressure chemical vapor deposition (LPCVD) furnace with 300 mTorr and a thin silicon dioxide (SiO₂) layer was deposited at 300 °C on top of the epi-Ge layer, as the gate insulator of the following Ge-MOS device. It was followed that the samples were divided into two groups for study in this work. In the first group, the supercritical fluid (SCF) treatment was performed right after the gate SiO₂ deposition to enhance the Ge-MOS device performance. The sample was placed in a SCF system at 150 °C for 1 h, where was injected with 2000–3000 psi of SCCO₂ fluid that were mixed with 5 vol % of propyl alcohol and 5 vol % of pure H₂O. The propyl alcohol acts as a surfactant between nonpolar-SCCO₂ fluid and polar-H₂O molecules, such that the H₂O molecules are uniformly distributed in SCCO₂ fluid and delivered into the gate SiO₂ film to passivate defect states. In the second group, the influence of PDA on the Ge MOS device characteristics was studied further. The sample after the gate SiO₂ deposition was subjected to a PDA process at 450 °C for 30 min in a vacuum furnace with 1 × 10⁻⁷ torr, and then the SCF post-treatment was implemented with the same conditions as mentioned above. Finally, aluminum electrodes were thermally evaporated on the

^{a)} Author to whom correspondence should be addressed. Electronic mail: ptliu@mail.nctu.edu.tw. Tel.: 886-3-5712121 ext. 52994. FAX: 886-3-5735601.

FIG. 1. The cross-sectional HRTEM images of LPCVD-SiO₂ on epi-Ge substrate (a) before and (b) after the treatment of 3000 psi SCCO₂ fluids mixed with 5 vol % of propyl alcohol and 5 vol % of pure H₂O at 150 °C.

top surface of SiO₂ film with an electrode area of 7.07×10^{-4} cm² and the back side of silicon wafer to fabricate Ge-MOS capacitors. The material analysis of x-ray photoelectron spectroscopy (XPS) on epi-Ge channel layer was also performed to examine the evolution of chemical bonding before and after SCCO₂ treatment. In order to clearly distinguish the gate insulator/epi-Ge interface for signal collection, the SCCO₂ process was applied to a stack structure of 13 nm thick HfO₂/epi-Ge layers. It is noted that the HfO₂ layer was *in situ* removed by Ar⁺ sputtering process before XPS spectra collection. Therefore, the information of chemical bonding at the epi-Ge surface can be obtained after SCF treatment.

Figures 1(a) and 1(b) show the cross-sectional high-resolution transmission electron microscopy (HRTEM) images for the LPCVD-SiO₂ film deposited on epi-Ge layer, before and after the SCCO₂ postgate dielectric treatment, respectively. In Fig. 1(a), the thickness of as-deposited SiO₂ film is observed to be about 13.5 nm. After immersion of SCCO₂ fluids with oxidant (H₂O molecule) at 150 °C for 1 h, the dielectric thickness above the Ge layer is increased to about 16.6 nm in total, and a clear and even interface is exhibited, as shown in Fig. 1(b). It is inferred that the increase of dielectric thickness and the even interface formed are originated from the formation of interfacial germanium oxide (GeO_x) during the SCF treatment with excellent permeability. The following XPS analysis results will support the inference.

The frequency dependence of capacitance-voltage (C-V) curves for the Ge-MOS device with various post-treatments is studied at 300 K, as depicted in Fig. 2(a). It is observed that the inversion capacitance which occurs at positive gate bias for p-type Ge exhibits frequency dispersion in different levels. The frequency dispersion behavior is attributed to the response of minority carrier generation from interface defect states to measuring frequencies. The fast minority-carrier response can be achieved at low frequency.¹² Compared with the case of lower interface state densities, the Ge-MOS capacitor with higher interface state densities also will present a larger inversion capacitance, and the gap of the inversion capacitances between both cases shrinks as the increase of measuring frequencies. In this work, the inversion capacitance of Ge-MOS device with SCF treatment declines fastest and approaches to an ideal minimum capacitance as compared to the one without SCF treatment, especially in the high measuring frequency of 500 KHz. In addition, it was shown that the C-V frequency dispersion decreased with in-

FIG. 2. (Color online) (a) The C-V characteristics of Ge-MOS devices with various SCF treatments. Electrical measurement with measuring frequencies of 10, 200, and 500 KHz was conducted at 25 °C, and (b) XPS spectra of Ge 3d signal on the epi-Ge channel layer with and without SCF treatment. The circles and the lines present the experimental data and peak fitting results, respectively. The inset indicates numerical intensity of chemical bonds by calculating the XPS peak area. It shows that the signal intensity of GeO₂ bonding increases after SCF treatment.

creasing the SCF pressure. It is reasonably believed that the solubility of oxidant (H₂O) and surfactant (propyl alcohol) is increased with increasing the CO₂ pressure.¹⁴ The increased pressure can also enhance the penetration of SCF to the interface between gate dielectric film and epi-Ge layer. Figure 2(b) shows XPS spectra of Ge 3d signal on the interface between gate dielectric layers and epi-Ge before and after SCF treatment. The detected signal of Ge 3d spectra primarily comes from the surface of epi-Ge channel layer, since the gate dielectric layer was *in situ* removed previously by Ar⁺ sputtering before XPS spectra collection. The signals of GeO_x and GeO₂ bonding were observed for both samples from the XPS analysis. For the sample without SCF process, it is inferred that the species of oxygen will oxidize the Ge surface to form loose native oxide layer during the early stage of gate dielectric film deposition. After SCF treatment,

FIG. 3. The C-V characteristics of 450 °C PDA-treated Ge-MOS devices before and after SCF post-treatments. The initial Ge-MOS device without PDA process was referred to as the control sample. The inset shows the gate leakage current density of PDA-treated Ge-MOS devices before and after SCF post-treatment.

higher signal intensity of GeO_2 bonding at the epi-Ge surface is observed obviously. The results reasonably explain that the oxidation at the epi-Ge/gate dielectric interface has occurred by adding oxidant (H_2O molecules) to the SCCO_2 fluid with excellent transport capacity. The formation of interfacial GeO_2 layer can smoothen the epi-Ge surface and alleviate frequency dispersion of inversion capacitance.

The thermal stability and the effects of SCF treatment on PDA-treated Ge-MOS device are investigated further for realistic Ge-MOSFET fabrication consideration. Figure 3 shows C-V characteristics of 450 °C PDA-treated Ge-MOS devices before and after SCCO_2 post-treatment. The inset of Fig. 3 also depicts the leakage current characteristics of the PDA-treated Ge-MOS devices before and after SCCO_2 post-treatment. The least accumulation capacitance is observed in the PDA-treated Ge-MOS device, about a 66% reduction compared with the control sample (without PDA process). The significant reduction of the accumulation capacitance due to poor charge holding capability can be attributed to the large leakage current of PDA-treated Ge MOS device, as shown in the inset of Fig. 3. It was reported that thermal process induces Ge decomposition and desorption into gate dielectric layer. The incorporation of Ge in dielectric insulator is believed to act as defect traps and thereby causes an increased gate leakage current.^{2,5,13} In this study, the implementation of SCF treatment after PDA process significantly reduces leakage current of gate insulator and recovers the C-V characteristic to a similar state as the initial Ge-MOS device without PDA process (control sample). This indicates

again that oxidant (H_2O molecule) is effectively transported into SiO_2 film by the high-pressure SCF and passivates the defect states generated in the Ge-MOS device during high-temperature thermal PDA process.

In summary, a low-temperature SCCO_2 process at 150 °C has been proposed to treat the gate oxide/epi-Ge interface and restore Ge-MOS device degradation after a high-temperature PDA process. It is observed that the uneven and poor interface was easily formed during thermal deposition processes on epi-Ge layer. After the SCF treatment, a smooth GeO_2 interface layer is formed and the frequency dispersion of inversion capacitance is alleviated. Furthermore, electrical degradation of Ge-MOS device after 450 °C PDA process leads to the reduction of accumulation capacitance and the increase of gate leakage current. The SCF treatment also can transport the oxidant into the gate dielectric layer and passivate the Ge-related defect states generated by PDA process. Electrical characteristics of Ge-MOS device are effectively recovered to an extent similar to the one before PDA process.

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- ¹S. Takagi, T. Maeda, N. Taoka, M. Nishizawa, Y. Morita, K. Ikeda, Y. Yamashita, M. Nishikawa, H. Kumagai, R. Nakane, S. Sugahara, and N. Sugiyama, *Microelectron. Eng.* **84**, 2314 (2007).
- ²H. Matsubara, T. Sasada, M. Takenaka, and S. Takagi, *Appl. Phys. Lett.* **93**, 032104 (2008).
- ³K. Prabhakaran, F. Maeda, Y. Watanabe, and T. Ogino, *Appl. Phys. Lett.* **76**, 2244 (2000).
- ⁴J. Oh and J. C. Campbell, *J. Electron. Mater.* **33**, 364 (2004).
- ⁵S. Van Elshocht, B. Brijs, M. Caymax, T. Conard, T. Chiarella, S. De Gendt, B. De Jaeger, S. Kubicek, M. Meuris, B. Onsia, O. Richard, I. Teerlinck, J. Van Steenberghe, C. Zhao, and M. Heyns, *Appl. Phys. Lett.* **85**, 3824 (2004).
- ⁶N. Lu, W. Bai, A. Ramirez, C. Mouli, A. Ritenour, M. L. Lee, and D. Antoniadis, *Appl. Phys. Lett.* **87**, 051922 (2005).
- ⁷Q. Zhang, N. Wu, D. M. Y. Lai, Y. Nikolai, L. K. Bera, and C. Zhu, *J. Electrochem. Soc.* **153**, G207 (2006).
- ⁸C. W. Wang, R. T. Chang, W. K. Lin, R. D. Lin, M. T. Liang, J. F. Yang, and J. B. Wang, *J. Electrochem. Soc.* **146**, 3485 (1999).
- ⁹P. T. Liu, C. T. Tsai, T. C. Chang, K. T. Kim, P. L. Chang, C. M. Chen, and H. F. Cheng, *Electrochem. Solid-State Lett.* **9**, G124 (2006).
- ¹⁰P. T. Liu, C. T. Tsai, T. C. Chang, K. T. Kim, P. L. Chang, C. M. Chen, and Y. C. Chen, *IEEE Trans. Nanotechnol.* **6**, 29 (2007).
- ¹¹P. T. Liu, C. T. Tsai, and P. Y. Yang, *Appl. Phys. Lett.* **90**, 223101 (2007).
- ¹²P. Batude, X. Garros, L. Clavelier, C. Le Royer, J. M. Hartmann, V. Loup, P. Besson, L. Vandroux, S. Deleonibus, and F. Boulanger, *Microelectron. Eng.* **84**, 2320 (2007).
- ¹³Y. Kamata, *Mater. Today* **11**, 30 (2008).
- ¹⁴C. T. Tsai, T. C. Chang, K. T. Kim, P. T. Liu, P. Y. Yang, C. F. Weng, and F. S. Huang, *J. Appl. Phys.* **103**, 074108 (2008).