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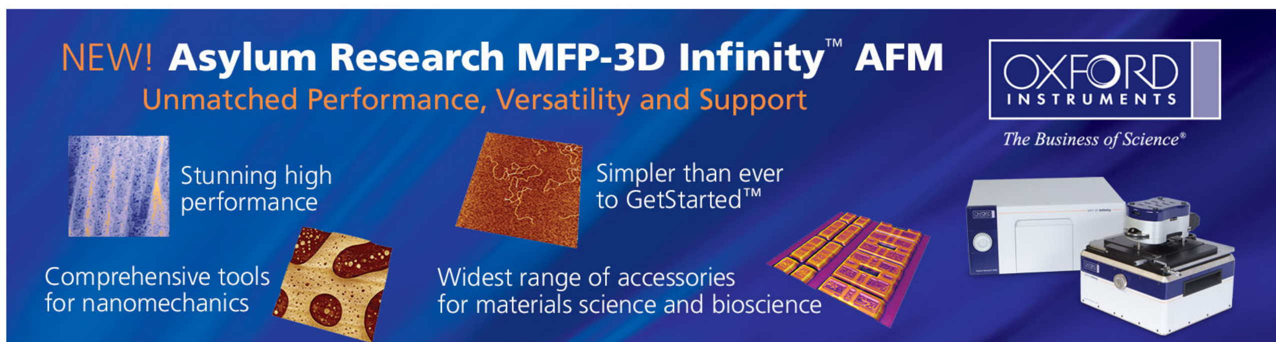

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Effects of postgate dielectric treatment on germanium-based metal-oxide-semiconductor device by supercritical fluid technology

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Supercritical fluid (SCF) technology is employed at low temperature as a postgate dielectric treatment to improve gate SiO_2/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 SiO_2/Ge interface at 150 °C. A smooth interfacial GeO_2 layer between gate SiO_2 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 (SiO_2) 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 GeO_2 formation.[2] In this study, a low-temperature supercritical CO_2 ($SCCO_2$) fluid technology is proposed as a postgate dielectric treatment at 150 °C to improve the SiO_2/Ge interface after high-temperature PDA process. The $SCCO_2$, 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 $SCCO_2$ fluid with specific surfactants. It is thereby allowed for $SCCO_2$ fluid to transport the oxidant and penetrates the dielectric layer for trap passivation and interface oxidation at low temperature.[9–11] The $SCCO_2$ fluid mixed with oxidant is proposed in this work for the formation of interfacial GeO_2 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 GeH_4 partial pressure of 8 Pa. Annealing under H_2 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 H_2 bake at 750 °C. This epitaxial Ge (epi-Ge) layer is p-type with an electrically activated concentration of 4×10^{15} cm^{-3}. The wafer was immediately loaded into a low-pressure chemical vapor deposition (LPCVD) furnace with 300 mTorr and a thin silicon dioxide (SiO_2) 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 SiO_2 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 $SCCO_2$ fluid that were mixed with 5 vol % of propyl alcohol and 5 vol % of pure H_2O. The propyl alcohol acts as a surfactant between nonpolar-$SCCO_2$ fluid and polar-H_2O molecules, such that the H_2O molecules are uniformly distributed in $SCCO_2$ fluid and delivered into the gate SiO_2 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 SiO_2 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

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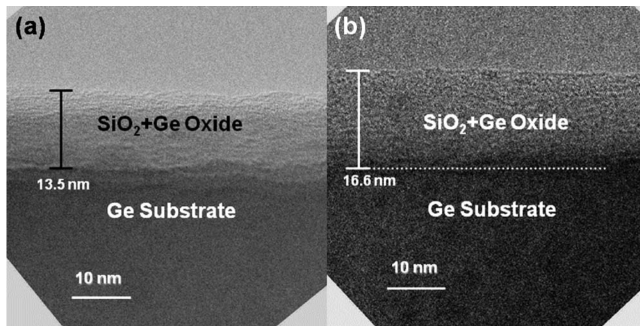
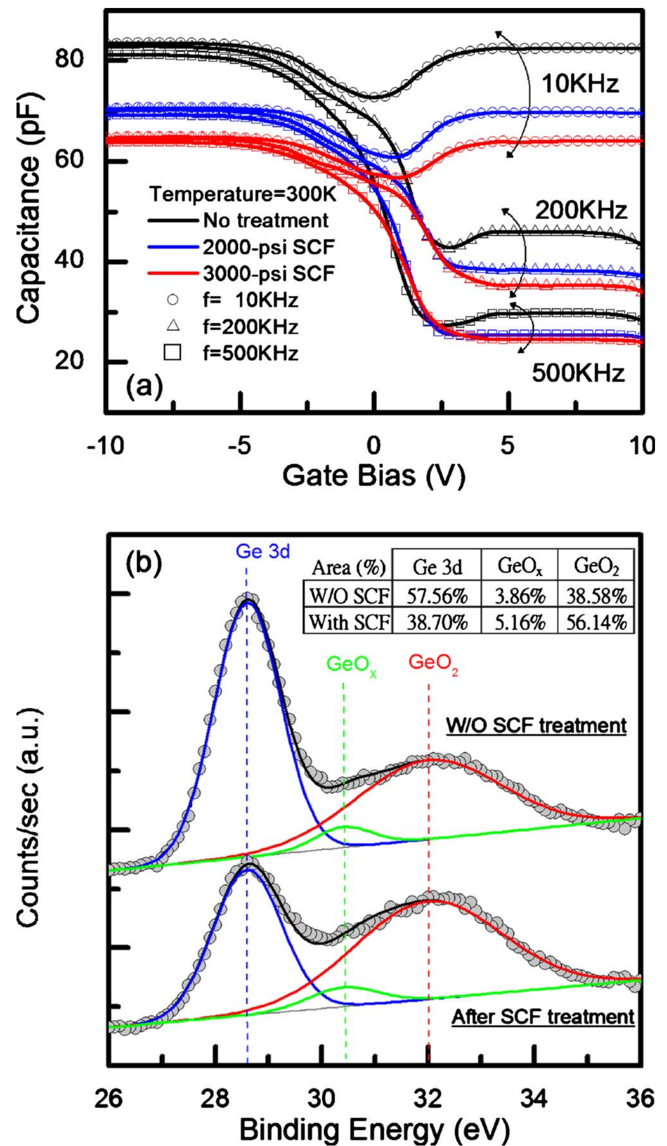


FIG. 1. The cross-sectional HRTEM images of LPCVD-SiO_2 on epi-Ge substrate (a) before and (b) after the treatment of 3000 psi $SCCO_2$ fluids mixed with 5 vol % of propyl alcohol and 5 vol % of pure H_2O at 150 °C.

top surface of SiO_2 film with an electrode area of 7.07×10^{-4} cm^2 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 $SCCO_2$ treatment. In order to clearly distinguish the gate insulator/epi-Ge interface for signal collection, the $SCCO_2$ process was applied to a stack structure of 13 nm thick HfO_2/epi-Ge layers. It is noted that the HfO_2 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-SiO_2 film deposited on epi-Ge layer, before and after the $SCCO_2$ postgate dielectric treatment, respectively. In Fig. 1(a), the thickness of as-deposited SiO_2 film is observed to be about 13.5 nm. After immersion of $SCCO_2$ fluids with oxidant (H_2O 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-



Area (%)	Ge 3d	GeO_x	GeO_2
W/O SCF	57.56%	3.86%	38.58%
With SCF	38.70%	5.16%	56.14%

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 3*d* 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 GeO_2 bonding increases after SCF treatment.

creasing the SCF pressure. It is reasonably believed that the solubility of oxidant (H_2O) and surfactant (propyl alcohol) is increased with increasing the CO_2 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 3*d* signal on the interface between gate dielectric layers and epi-Ge before and after SCF treatment. The detected signal of Ge 3*d* 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 GeO_2 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,

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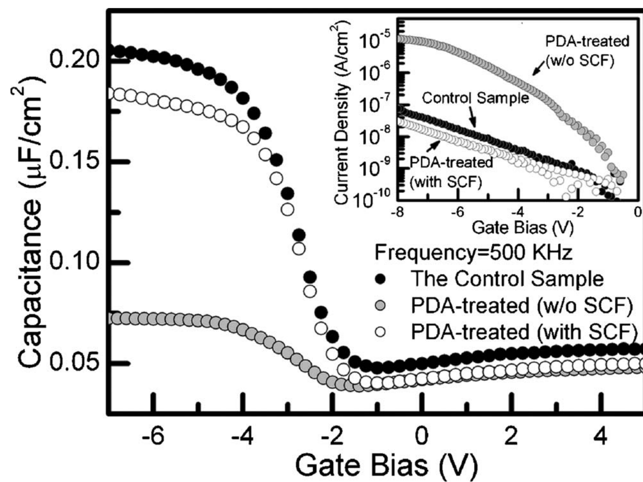

FIG. 3. The C-V characteristics of 450 °C PDA-treated Ge-MOS devices before and after SCF post-treatments. The initial Ge-MOS device without PDA process was referred to as the control sample. The inset shows the gate leakage current density of PDA-treated Ge-MOS devices before and after SCF post-treatment.

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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