

## Chapter 2

# Application of Supercritical Fluid Technology on Metal-Oxide Dielectric Thin Film

### 2.1 Fabrication of Metal-Insulator-Silicon and Experiment Process

In this experiment, a metal-oxide  $\text{HfO}_2$  film layer was deposited on p-type (100) silicon wafers by reactive DC magnetron sputtering at room temperature under  $\text{Ar}/\text{O}_2$  ambient. The thickness of as-deposited  $\text{HfO}_2$  films was 7nm, which was measured by an ellipsometer system. Subsequently, the wafers with 7nm-thick  $\text{HfO}_2$  film were split into three groups, and processed with different post-treatments to study the properties of low-temperature-deposited  $\text{HfO}_2$  film. The first group labeled as Baking-only treatment, was designed as the control sample, and was only baked on a hot plate at 150 °C for 2 hrs. The second group labeled as  $\text{H}_2\text{O}$  vapor treatment, was immersed into a pure  $\text{H}_2\text{O}$  vapor ambience at 150 °C for 2 hrs in a pressure-proof stainless steel chamber with a volume of 30cm<sup>3</sup>. The third group marked as 1500~3000psi- $\text{SCCO}_2$  treatment, was placed in the supercritical fluid system at 150°C for 2 hrs, where was injected with 1500~3000psi of  $\text{SCCO}_2$  fluids mixed with 5 vol.% of propyl alcohol and 5 vol.% of pure  $\text{H}_2\text{O}$ . The propyl alcohol plays a role of surfactant between nonpolar- $\text{SCCO}_2$  fluids and polar- $\text{H}_2\text{O}$  molecules, so that the  $\text{H}_2\text{O}$  molecule uniformly distributes in  $\text{SCCO}_2$  fluids and be delivered into the  $\text{HfO}_2$  film for passivating defects. The supercritical fluid system is shown in Fig. 2-1.

After these different treatments, the thickness of  $\text{HfO}_2$  films is almost intact, checked with the ellipsometer measurement. Fourier transformation infrared spectroscopy (FTIR) and thermal desorption spectroscopy (TDS) were also used to investigate the evolution of chemical functional bonding and the content of oxygen in  $\text{HfO}_2$  films, respectively. Electrical measurements were conducted on metal insulator semiconductor (MIS) capacitors by thermally evaporating Al electrodes on the front

surface of the HfO<sub>2</sub> films and the backside of the silicon wafer. The current density-electric field (*J-E*) characteristics, capacitance-voltage (*C-V*) characteristics, breakdown voltage and gate bias stress were measured with HP4156C semiconductor parameter analyzer for investigating the transformation of HfO<sub>2</sub> film. The experiment processes of thin HfO<sub>2</sub> film with various treatments are exhibited in Fig. 2-2.

## 2.2 Analysis of Material and Discussion

### 2.2.1 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

Figure 2-3 (a) shows the FTIR spectra of HfO<sub>2</sub> films after various post-treatments, including Baking-only, H<sub>2</sub>O vapor and 3000 psi-SCCO<sub>2</sub> treatment. The functional group referred to Hf-O-Hf bonding is at 509 cm<sup>-1</sup> and 690 cm<sup>-1</sup>, and the absorption peak at around 1070 cm<sup>-1</sup> attributes to the Si-O-Si bond. The Si-O-Si bond originates from the formation of interface layer (SiO<sub>x</sub>) between HfO<sub>2</sub> film and silicon wafer during fabricating HfO<sub>2</sub> films in Ar/O<sub>2</sub> ambient. The peak intensity of Si-O-Si bond for different treatments is almost the same, meaning that these post-treatments would not make different influence on the thickness and quality of the interfacial SiO<sub>x</sub> film. For the H<sub>2</sub>O-vapor-treated HfO<sub>2</sub> film, however, the peak intensity of Hf-O-Hf bands (509 cm<sup>-1</sup> and 690 cm<sup>-1</sup>) raises apparently in comparison with the baking-only-treated HfO<sub>2</sub> film. This is believed well that the H<sub>2</sub>O vapor would permeate into HfO<sub>2</sub> film and makes reaction with Hf dangling bonds (i.e. traps) forming Hf-O-Hf bands. These traps in the low-temperature deposited HfO<sub>2</sub> film could be thereby passivated by H<sub>2</sub>O vapor molecules. Furthermore, with 3000 psi-SCCO<sub>2</sub> treatment, obvious increase in the intensity of Hf-O-Hf bonding is observed in the FTIR. It indicates that the best transport efficiency of H<sub>2</sub>O molecules into HfO<sub>2</sub> film is achieved by the SCCO<sub>2</sub> fluids, potentially modifying the dielectric properties of HfO<sub>2</sub> film, and the transporting mechanism for SCCO<sub>2</sub> fluids taking H<sub>2</sub>O molecule into HfO<sub>2</sub> film is shown in Fig. 2-4.

Figure 2-3 (b) shows the FTIR spectra of HfO<sub>2</sub> films after SCCO<sub>2</sub> treatment under different pressure. In Fig. 2-3 (b), the intensity of Hf-O-Hf bands (509 cm<sup>-1</sup> and 690 cm<sup>-1</sup>) grows as the pressure of SCCO<sub>2</sub> fluids increases, and the best improvement is obtained for 3000 psi-SCCO<sub>2</sub> treatment. It could be referred to that the capability for SCCO<sub>2</sub> fluids to dissolve co-solvent (5 vol.% of propyl alcohol and 5 vol.% of pure H<sub>2</sub>O) would be advanced under higher pressure, and the better diffusion ratio into thin films is also reasonable when raising pressure[21, 22]. Therefore, the SCCO<sub>2</sub> fluids mixed with co-solvent would completely infiltrate in into HfO<sub>2</sub> films as the pressure increasing from 1500 psi to 3000 psi, and the best improvement for HfO<sub>2</sub> films is achieved because of advancing the reaction probability between H<sub>2</sub>O molecule and Hf dangling bonds.

### **2.2.2 Thermal Desorption System – Atmospheric Pressure Ionization Mass Spectrometer (TDS-APIMS) Analysis**

The TDS measurement, as shown in the Fig. 2-5, was carried out upon heating these treated HfO<sub>2</sub> films from 50 to 800 °C at a heating rate of 10 °C/min in vacuum (10<sup>-5</sup> Pa.). In Fig. 2-5 (a), m/e (mass-to-charge ratio) = 32 peak that is attributed to O<sub>2</sub> was monitored to evaluate the content of oxygen outgassing form HfO<sub>2</sub> films. It is clearly found the highest oxygen content is detected in the 3000 psi-SCCO<sub>2</sub> treated HfO<sub>2</sub> film, certainly consistent with the FTIR observation. From Fig. 2-5 (b), m/e (mass-to- charge ratio) = 18 peak that is attributed to H<sub>2</sub>O, the residual moisture in HfO<sub>2</sub> is minimized after 3000 psi-SCCO<sub>2</sub> treatment. This is result from SCCO<sub>2</sub> fluid not only employed to transport the H<sub>2</sub>O molecule into HfO<sub>2</sub> film but a suitable method to remove H<sub>2</sub>O molecule in addition [21, 22].

### **2.2.3 X-ray Photoelectron Spectroscopy (XPS) Analysis**

XPS involves measuring the photoelectron spectra obtained when a sample surface is irradiated with x-rays. The kinetic energy (peak position) of the

photoelectrons can be written as

$$E_K = h\nu - E_B - \phi_s - q\phi$$

where  $h\nu$  is the x-ray energy,  $E_B$  is the binding energy (the difference between the Fermi level and the energy level being measured),  $\phi_s$  is the work function of the electron spectrometer,  $q$  is the electronic charge, and  $\phi$  is the surface potential.

We have also performed XPS measurements using an Al  $K\alpha$  X-ray source (1486.6 eV photons) to determine the bonding environments of the Hf and O atoms. Figure 2-6 shows the XPS spectra for Hf 4f level that were calibrated from C 1s peak at 284.5 eV. Each spectrum was represented the result at different post-treatments, including Baking-only, H<sub>2</sub>O vapor and 3000psi-SCCO<sub>2</sub> treatment. The first group labeled as Baking-only treatment, was designed as the control sample, and was only baked on a hot plate at 150 °C for 2 hrs. The second group labeled as H<sub>2</sub>O vapor treatment, was immersed into a pure H<sub>2</sub>O vapor ambience at 150 °C for 2 hrs in a pressure-proof stainless steel chamber with a volume of 30cm<sup>3</sup>. The third group marked as 3000psi-SCCO<sub>2</sub> treatment, was placed in the supercritical fluid system at 150°C for 2 hrs, where was injected with 3000psi of SCCO<sub>2</sub> fluids mixed with 5 vol.% of propyl alcohol and 5 vol.% of pure H<sub>2</sub>O. As shown in Figure 2-6 , the Hf 4f<sub>5/2</sub> and Hf 4f<sub>7/2</sub> peaks, which have binding energies of 17.50 and 15.88 eV, respectively related to Hf-O bonding in HfO<sub>2</sub>. However, the binding energy of Hf 4f<sub>2/5</sub> peak shown in Figure 2-6 varied from 17.50 eV for Baking-only sample to 18.01 eV for 3000psi-SCCO<sub>2</sub> treatment sample. The origins of binding energy shift ( $\Delta$ BE) are suggested as a number of factors such as charge transfer effect, presence of electric field, environmental charge density, and hybridization. Among these, charge transfer is regarded as a dominant mechanism causing a binding energy shift. According to the charge transfer mechanism, removing an electron from the valence orbital generates the increment in core electron's potential and finally leads a chemical binding energy shift [23]. Therefore, it is considered that the Hf 4f<sub>5/2</sub> and Hf 4f<sub>7/2</sub> peaks shift originated from the enhanced charge transfer with different post-treatments, *i.e.*, the

larger portion of Hf atoms was fully oxidized with *3000psi-SCCO<sub>2</sub> treatment*. Figure 2-7 shows the O 1s core level peaks also demonstrated binding energy shift with changing of different post-treatments. Each peak can be split into two sub-peaks by Gaussian fitting which represent the Hf-O bonding at ~530.1 eV and O-Si bonding at ~531.5 eV [24,25]. The peak intensity of O-Si bond for different treatments is almost the same, meaning that these post-treatments would not make different influence on the thickness and quality of the interfacial SiO<sub>x</sub> film. For the H<sub>2</sub>O-vapor-treated HfO<sub>2</sub> film, however, the peak intensity of Hf-O bands raises apparently in comparison with the baking-only-treated HfO<sub>2</sub> film. This is believed well that the H<sub>2</sub>O vapor would permeate into HfO<sub>2</sub> film and makes reaction with Hf dangling bonds (i.e. traps) forming Hf-O bands. These traps in the low-temperature deposited HfO<sub>2</sub> film could be thereby passivated by H<sub>2</sub>O vapor molecules. Furthermore, with SCCO<sub>2</sub> treatment, obvious increase in the intensity of Hf-O bonding is observed in the XPS. It indicates that the best transport efficiency of H<sub>2</sub>O molecules into HfO<sub>2</sub> film is achieved by the SCCO<sub>2</sub> fluids, potentially modifying the dielectric properties of HfO<sub>2</sub> film, and the transporting mechanism for SCCO<sub>2</sub> fluids taking H<sub>2</sub>O molecule into HfO<sub>2</sub> film is shown in Fig. 2-4. Summary of binding energies for HfO<sub>2</sub> films are shown in Table 2-1 and Table 2-2.

#### **2.2.4 Auger Electron Spectroscopy (AES) Analysis**

In order to analyze the composition of the hafnium oxide film after various post-treatments, including Baking-only, H<sub>2</sub>O vapor and 3000 psi-SCCO<sub>2</sub> treatment, we performed the Auger electron spectroscopy analysis. The first group labeled as Baking-only treatment, was designed as the control sample, and was only baked on a hot plate at 150 °C for 2 hrs. The second group labeled as H<sub>2</sub>O vapor treatment, was immersed into a pure H<sub>2</sub>O vapor ambience at 150 °C for 2 hrs in a pressure-proof stainless steel chamber with a volume of 30cm<sup>3</sup>. The third group marked as 3000psi-SCCO<sub>2</sub> treatment, was placed in the supercritical fluid system at 150°C for 2

hrs, where was injected with 3000psi of SCCO<sub>2</sub> fluids mixed with 5 vol.% of propyl alcohol and 5 vol.% of pure H<sub>2</sub>O. The propyl alcohol plays a role of surfactant between nonpolar-SCCO<sub>2</sub> fluids and polar-H<sub>2</sub>O molecules, so that the H<sub>2</sub>O molecule uniformly distributes in SCCO<sub>2</sub> fluids and be delivered into the HfO<sub>2</sub> film for passivating defects. As shown in Figure 2-8, the baking-only-treated and H<sub>2</sub>O vapor-treated films has oxygen composition lower than that of the hafnium oxide film after 3000 psi-SCCO<sub>2</sub> treatment. The propyl alcohol plays a role of surfactant between nonpolar-SCCO<sub>2</sub> fluids and polar-H<sub>2</sub>O molecules, so that the H<sub>2</sub>O molecule uniformly distributes in SCCO<sub>2</sub> fluids and be delivered into the HfO<sub>2</sub> film for passivating defects.

### 2.2.5 Transmission Electron Microscopy (TEM) Analysis

Figure 2-9 (a), (b), (c) show the influence of various post-treatments on HfO<sub>2</sub> thin film samples in TEM material analysis. The first group labeled as Baking-only treatment, was designed as the control sample, and was only baked on a hot plate at 150 °C for 2 hrs. The second group labeled as H<sub>2</sub>O vapor treatment, was immersed into a pure H<sub>2</sub>O vapor ambience at 150 °C for 2 hrs in a pressure-proof stainless steel chamber with a volume of 30cm<sup>3</sup>. The third group marked as 3000psi-SCCO<sub>2</sub> treatment, was placed in the supercritical fluid system at 150°C for 2 hrs, where was injected with 3000psi of SCCO<sub>2</sub> fluids mixed with 5 vol.% of propyl alcohol and 5 vol.% of pure H<sub>2</sub>O. The interfacial layer of SiO<sub>x</sub> for different treatments is almost the same. It is found that 3000psi-SCCO<sub>2</sub> treatment can improve performance of MIS, including leakage current density suppression and EOT reduction. On the other hand, the k value of Baking-only-treated, H<sub>2</sub>O-vapor-treated and 3000psi-SCCO<sub>2</sub>-treated HfO<sub>2</sub> film is about 20.4, 24.8 and 29.4. The k value is increased and interfacial layer is almost the same. It can be understood reasonably that during 3000psi-SCCO<sub>2</sub>-treated HfO<sub>2</sub> film is dense and thickness of interfacial layer is increasing a little due to oxygen penetration. The detail discussion would be in 2.3.3.

## 2.3 Analysis of Electrical Characteristics and Discussion

### 2.3.1 The current density-electric field ( $J$ - $E$ ) characteristics

The leakage current densities of HfO<sub>2</sub> films after different treatments are shown as a function of applied negative gate bias voltage in Fig. 2-11. Among various post-treatments, the baking-treated HfO<sub>2</sub> film exhibits the most serious leakage current, inferentially due to its poor dielectric characteristics with numerous traps inside the HfO<sub>2</sub> film and the interface between parasitical SiO<sub>x</sub> and Si wafer. The improvement of electrical characteristics is observed by using H<sub>2</sub>O vapor process, however, a high leakage current density still appears at larger applied voltages. It could be inferred reasonably dependent on the defect passivation efficiency. The most indicating that H<sub>2</sub>O vapor can passivate the traps (or defects) and alter dielectric properties of the low-temperature-deposited HfO<sub>2</sub> film. After H<sub>2</sub>O vapor treatment, effective improvement of electrical characteristic is obtained by the 3000 psi-SCCO<sub>2</sub> treatment, exhibiting the lowest leakage current density among all samples. Low leakage current density ( $\sim 2 \times 10^{-7}$  A/cm<sup>2</sup>) is kept constantly, even biased at an electric field of 3 MV/cm. The electrical performance agrees with FTIR analysis, in which 3000 psi-SCCO<sub>2</sub> treatment modified HfO<sub>2</sub> dielectrics even effectively.

### 2.3.2 Conduction Mechanism

There may be different conduction mechanisms in the insulator thin film, including Schottky-Richardson emission [35], Frenkel-Poole emission [35,36], Fowler-Nordheim tunneling [35,36], and trap assisted tunneling [37,38] illustrated in Fig 2-10. The Schottky-Richardson emission generated by the thermionic effect is caused by the electron transport across the potential energy barrier via field-assisted lowering at a metal-insulator interface. The leakage current governed by the Schottky-Richardson emission is as following:

$$J_{SR} = A^* T^2 \exp\left(\beta_{SR} E^{1/2} - \phi_{SR} / k_B T\right)$$

where  $\beta_{SR} = (q^3 / 4\pi\epsilon_0\epsilon)^{1/2}$ ,  $q$  is the electronic charge,  $A^*$  is the effective Richardson constant,  $\phi_{SR}$  is the contact potential barrier,  $E$  is the applied electric field,  $\epsilon_0$  is the permittivity in vacuum,  $\epsilon$  is the high frequency relative dielectric constant,  $T$  is the absolute temperature, and  $k_B$  is the Boltzmann constant. We can find the slope of the leakage current equation.

$$\ln J_{SR} = \beta_{SR} E^{1/2} / k_B T + [\ln(A^* T^2) - \phi_{SR} / k_B T]$$

$$\text{Solpe} = \beta_{SR} / k_B T$$

The Frenkel-Poole emission is due to field-enhanced thermal excitation of trapped electrons in the insulator into the conduction band. The leakage current equation is:

$$J_{FP} = J_0 \exp\left(\beta_{FP} E^{1/2} - \phi_{FP} / k_B T\right)$$

where  $J_0 = \sigma_0 E$  is the low-field current density,  $\sigma_0$  is the low-field conductivity,  $\beta_{FP} = (q^3 / \pi\epsilon_0\epsilon)^{1/2}$ ,  $q$  is the electronic charge,  $\phi_{FP}$  is the contact potential barrier,  $E$  is the applied electric field,  $\epsilon_0$  is the permittivity in vacuum,  $\epsilon$  is the high frequency relative dielectric constant,  $T$  is the absolute temperature, and  $k_B$  is the Boltzmann constant. We can find the slope of the leakage current equation.

$$\ln J_{FP} = \beta_{FP} E^{1/2} / k_B T + [\ln(J_0) - \phi_{FP} / k_B T]$$

$$\text{Solpe} = \beta_{FP} / k_B T$$

The Fowler-Nordheim tunneling is the flow of electrons through a triangular potential barrier. Tunneling is a quantum mechanical process similar to throwing a ball against a wall often results that the ball goes through the wall without damaging the wall or the ball. It also loses no energy during the tunnel event. The probability of this event happening, however, is extremely low, but an electron incident on a barrier typically several nm thick has a high probability of transmission. The Fowler-Nordheim tunneling current  $I_{FN}$  is given by the expression [39]:



$$I_{FN} = A_G A_{FN} \varepsilon_{ox}^2 \exp(-B_{FN} / \varepsilon_{ox})$$

where the  $A_G$  is the gate area,  $\varepsilon_{ox}$  is the oxide electric field, and  $A_{FN}$  and  $B_{FN}$  are usually considered to be constant.  $A_{FN}$  and  $B_{FN}$  are given as the following:

$$A_{FN} = q^3 (m/m_{ox}) / 8\pi h \Phi_B = 1.54 \times 10^{-6} (m/m_{ox}) / \Phi_B$$

$$B_{FN} = 8\pi (2m_{ox} \Phi_B^3)^{1/2} / 3eh = 6.83 \times 10^7 [(m/m_{ox}) \Phi_B^3]^{1/2}$$

where  $m_{ox}$  is the effective electron mass in the oxide,  $m$  is the free electron mass,  $q$  is the electronic charge, and  $\Phi_B$  is the barrier height at the silicon-oxide interface given in units of eV in the expression for  $B_{FN}$ .  $\Phi_B$  is actually an effective barrier height that take into account barrier height lowering and quantization of electrons at the semiconductor surface. Rearranging  $I_{FN}$  formula gives by:

$$\ln(I_{FN} / A_G \varepsilon_{ox}^2) = \ln(J_{FN} / \varepsilon_{ox}^2) = \ln(A_{FN}) - B_{FN} / \varepsilon_{ox}$$

A plot of  $\ln(J_{FN} / \varepsilon_{ox}^2)$  versus  $(I / \varepsilon_{ox}^2)$  should be a straight line if the conduction through the oxide is pure Fowler-Nordheim conduction [39].

In the trap assisted tunneling model, it is assumed that electrons first tunnel through the SiO<sub>x</sub> interfacial layer (direct-tunneling). Then, electrons tunnel through traps located below the conduction band of the high-k thin film and leak to substrate finally [37]. The equation of leakage current density is [38]:

$$J = \alpha / E_{ox} \exp(-\beta / E_{ox})$$

From the equations as shown above, leakage current behaviors of insulate films can be investigated further on the leakage current density  $J$  electric field  $E$  characteristics such as  $J$  vs.  $E^{1/2}$  plots.

The plot of the nature log of leakage current density versus the square root of the applied electric field was observed. It is found that the leakage current density is linearly related to square root of the applied electric field. The linear variations of the current correspond either to Schottky-Richardson emission or to Frenkel-Poole conduction mechanism. For trap states with coulomb potentials, the expression is

virtually identical to that of the Schottky-Richardson emission. The barrier height, however, is the depth of the trap potential well, and the quantity  $\beta_{FP}$  is larger than in the case of Schottky-Richardson emission by a factor of 2.

Leakage conduction mechanism is also investigated to support the comments on the electrical improvement of HfO<sub>2</sub> film. Fig. 2-12(a) plots  $\ln(J/E)$  versus reciprocal of electric field variation for the baking-only treated HfO<sub>2</sub> film, and a schematic energy band diagram accounting for leakage transport mechanism shown in the inset. A good linear fitting explains Fowler-Nordheim (F-N) tunneling [40] occurs in the electric fields higher than 0.7 MV/cm. Also, it is consistent with the electrical behavior of baking-only treated HfO<sub>2</sub> film in Fig. 2-11 that leakage current density sharply increases, while gate bias voltage larger than 0.7 MV/cm. This could be attributed to the trap-assisted tunneling due to numerous traps inside the 150°C-baking treated HfO<sub>2</sub> film [41]. For the 3000 psi-SCCO<sub>2</sub> treated HfO<sub>2</sub> film, a plot of leakage current density versus the square root of the applied field ( $E^{1/2}$ ) gives a good representation of the leakage behavior at high electric fields, as shown in Fig. 2-12(b). The leakage current density of the 3000 psi-SCCO<sub>2</sub> treated HfO<sub>2</sub> is linearly related to the square root of the applied electric field, demonstrating Schottky-Richardson emission transport mechanism [42]. The Schottky-type conduction can be verified by comparing the theoretical value of  $\beta_{SR} = (q^3 / 4\pi\epsilon_0\epsilon)^{1/2}$  with the calculated one obtained from the slope of the experimental curve  $\ln J$  versus  $E^{1/2}$  [43], where  $q$  is the electronic charge,  $\epsilon_0$  the dielectric constant of free space,  $\epsilon$  is the high frequency relative dielectric constant. The Schottky emission generated by the thermionic effect is caused by electron transport across the potential energy barrier via field-assisted lowering at a metal-insulator interface, shown in the insert of Fig. 2-12(b), and independent of traps. From the slope of  $\ln J$  versus  $E^{1/2}$ , the calculated value of relative dielectric constant ( $\epsilon$ ) is 26.4, and which is close to the determined value of 29.4 in capacitance-voltage ( $C-V$ ) measurement (referring to table 2-3). This also proves, for 3000psi-SCCO<sub>2</sub> treated HfO<sub>2</sub> film, the conduction mechanism is really Schottky emission, but not trap-dependent Poole-Frenkel emission [43]. Additionally,

the evolution of conduction mechanisms from trap-assisted tunneling to Schottky emission can confirm these defects inside low-temperature-deposited HfO<sub>2</sub> film is minimized effectively by implementing the proposed SCCO<sub>2</sub> technology. With SCCO<sub>2</sub> treatment under different pressure, the leakage current densities of HfO<sub>2</sub> films at negative gate bias are shown in Fig. 2-13 (a). It is obviously discovered that the restraint of leakage current is advanced with SCCO<sub>2</sub> treatment under larger pressure. For further analysis, the leakage conduction mechanism of HfO<sub>2</sub> films, after the SCCO<sub>2</sub> treatment under different pressure, are discussed in addition. Figure 2-13 (b) shows the plot of  $\ln(J/E)$  versus  $E^{1/2}$ , which is according to Poole-Frenkel emission, and inset is the energy band diagram for representing this trap-dependent leakage transport mechanism [43]. In Fig. 2-13 (b), for 1500 psi-SCCO<sub>2</sub> treated HfO<sub>2</sub> film, the linear representation occurs from small electric field (or applied gate bias). This indicates that the traps in HfO<sub>2</sub> film could be reduced by 1500psi-SCCO<sub>2</sub> treatment, and the conduction mechanism is improved first from trap-assisted tunneling to Poole-Frenkel emission. However, it is not accomplished due to the partial traps remain and lead to poorer dielectric characteristic. Adding pressure of SCCO<sub>2</sub> treatment, the Poole-Frenkel emission is gradually restrained, and finally replaced by Schottky emission with 3000 psi-SCCO<sub>2</sub> treatment, exactly as above description. It implies that more efficient trap-passivation and fewer traps in HfO<sub>2</sub> films are achieved with SCCO<sub>2</sub> treatment under higher pressure, and thereby the leakage current of HfO<sub>2</sub> film decreases apparently as raising the pressure of SCCO<sub>2</sub> treatment. Besides, the similar movement is also corresponding to the results of FTIR spectra in Fig. 2-3 (b). The leakage current densities of HfO<sub>2</sub> films after different treatments are shown as a function of applied positive gate bias voltage in Fig. 2-14, and the lower leakage current still could be acquired after 3000 psi-SCCO<sub>2</sub> and H<sub>2</sub>O vapor treatment, especially treated with SCCO<sub>2</sub> fluids. This could be attributed to the influence of traps in the interface between parasitical SiO<sub>x</sub> and Si wafer. Generally, in positive gate bias, the sources of electron are (1) the interface states, (2) defects in depletion region, (3) back electrode of substrate, [45] and the later two source are negligible due to the

p-type signal-crystal Si wafer is used in this work. For baking-only treated HfO<sub>2</sub> film, the great quantity of interface states still exist which generate electron-hole pair and lead to higher leakage current, as described in the inset of Fig. 2-14. After 3000 psi-SCCO<sub>2</sub> treatment, the interface states were deactivated, hence the leakage current is reduced. The reduction of interface states would be proved in capacitance-voltage measurement.

### 2.3.3 The capacitance-voltage (C-V) characteristics

The capacitance-voltage (C-V) characteristics are also generally used to judge the quality of dielectric films. Figure 2-15 shows capacitance-voltage characteristics of HfO<sub>2</sub> films after different treatment, measuring at 1M Hz with gate bias swing from negative voltage to positive voltage (forward) and from positive voltage to negative voltage (reverse). The slope of C-V curve in transient region, i.e. from C<sub>max</sub> to C<sub>min</sub>, is relative to the interface states, for example, the sharp slope indicates fewer defects exist in the interface between HfO<sub>2</sub> and Si wafer. In Fig. 2-15, the baking-treated HfO<sub>2</sub> film presents the worst C-V curve and lower capacitance. This expresses the larger number of interface states exist and lead to the smooth C-V curve. Additionally, the lower dielectric constant, as shown in table 2-3, could be referred to the influence of defects in HfO<sub>2</sub> film. With H<sub>2</sub>O vapor treatment, the sharper C-V curve and higher capacitance are obtained, and it could be attributed to the reduction of defects in HfO<sub>2</sub> film and the interface. Furthermore, the best improvement is achieved by 3000 psi-SCCO<sub>2</sub> treatment. This exhibits that the SCCO<sub>2</sub> treatment possesses excellent ability to passivate the defects, including Hf dangling bonds and interface states.

Besides, from Fig. 2-15, the shift of C-V curve under forward and reverse swing is also appears in baking-treated and H<sub>2</sub>O vapor-treated HfO<sub>2</sub> films. It is resulted from the trapped carrier in defects of HfO<sub>2</sub> films, and that is not expected for gate insulator of transistors. Under negative gate bias, the electric inject from Al gate into HfO<sub>2</sub> films and trapped by defects, leading to the larger gate bias is required for inducing

electron-inversion layer. For describing clear, we define the flat-band voltage is the gate bias as  $C/C_{\max} = 0.5$ , and the shift of the flat-band voltages under forward and reverse swing is shown in table 2-3. It is evidently observed that the baking-treated  $\text{HfO}_2$  film hold numerous defects because of the extensive shift of flat-band voltage, and the defects almost disappear after 3000 psi- $\text{SCCO}_2$  treatment.

These results conform to the tendency in current-voltage characteristics and again verify that the  $\text{SCCO}_2$  technology could effectively deactivate defects in  $\text{HfO}_2$  films.

Another interesting detection, in Fig. 2-15, is the change of flat-band voltage of different-treated  $\text{HfO}_2$  films under forward swing, also shown in table 2-3. For baking- treated  $\text{HfO}_2$  film, the flat-band voltage (= -3.2 volt.) is away from ideal gate bias voltage (about 0~0.3 volt.), and that of 3000 psi- $\text{SCCO}_2$  treated  $\text{HfO}_2$  is zeroed nearly. The main reason could be referred to (1) the positively charged Hf dangling bonds are passivated, (2) the fixed positive charges are removed by  $\text{SCCO}_2$  fluids. The mechanism of extracting of fixed charge is shown in Fig. 2-16, including positive and negative fixed charge [44]. The polarized- $\text{H}_2\text{O}$  molecule is taken as a dipole which would attract the fixed charge in  $\text{HfO}_2$  films. Afterward, the  $\text{H}_2\text{O}$  molecule and fixed charge are carried away by  $\text{SCCO}_2$  fluids mixed with propyl alcohol. For  $\text{H}_2\text{O}$  vapor-treated  $\text{HfO}_2$  film, the un-zeroed flat-band voltage could be attributed to (1) partial positively charged Hf dangling bonds remain, (2) the poorer capability for  $\text{H}_2\text{O}$  vapor to remove fixed charge. Hence, it is necessary for  $\text{H}_2\text{O}$  molecule to be driven into  $\text{HfO}_2$  films and carried away by  $\text{SCCO}_2$  fluids.

As a matter of fact, upon reducing the oxide thickness, it is difficult to calculate the density of interface states by using the high-low frequency method because of the substantially increased gate leakage current. Therefore, the interface capacitance ( $C_{it}$ ) was employed instead of interface states to investigate the interfacial property.

Figure 2-17 (a) and (b) illustrates the equivalent capacitance models of MOS structure without and with  $C_{it}$ , respectively [45]. For higher measuring frequency, fewer interface states could respond to the ac switching signal, so suiting to the model

in Fig. 2-17 (a) and presenting lower measured capacitance. For lower measuring frequency, more interface states could respond to the ac switching signal, so suiting to the model in Fig. 2-17 (b) and presenting higher measured capacitance. Therefore, the separation of  $C_{\max}$  under different measuring frequency appears if the interface states existing. Figure 2-18 shows the capacitance-voltage characteristics of HfO<sub>2</sub> films after different treatment, measuring at 1M Hz and 100k Hz with forward gate bias swing. A conspicuous separation occurs in baking-treated HfO<sub>2</sub> films, and the higher density of interface states is supposed. However, with 3000 psi-SCCO<sub>2</sub> treatment, the value of  $C_{\max}$  has only very slight rise under different measuring frequency, proofing that the effectively reducing interface states during SCCO<sub>2</sub> process. The sharp slope in transient region of C-V curve thereby is also reasonable.

#### 2.3.4 Breakdown voltage measurement and gate bias stress

Figure 2-19 (a), (b) show the breakdown characteristic curves of HfO<sub>2</sub> films after various treatments at positive and negative gate bias region, individually. The breakdown voltage is mainly relative to the qualities of dielectric films and the density of defects in the dielectric films. A large number of traps lead to the trap-assisted tunneling early occurs and a high leakage current appears at small electric field, such that the lower breakdown voltages of dielectric films comes up. In Fig. 2-20 (a) and (b), whether at negative or positive gate bias, the baking-treated HfO<sub>2</sub> film presents the worst performance in breakdown voltage because of the high density of defects, and the improvements of breakdown voltage are gradually achieved via H<sub>2</sub>O vapor and 3000 psi-SCCO<sub>2</sub> treatment. This result exhibits clearly that the density of defects in HfO<sub>2</sub> films are effectively reduced, and the breakdown voltage of 7nm HfO<sub>2</sub> film thereby could be substantially ameliorated from 1 V to 24 V at negative gate bias, from 30 V to 55 V at positive gate bias. It also indicates that the SCCO<sub>2</sub> fluids technology is greatly useful to enhance the low-temperature

deposited HfO<sub>2</sub> films by passivating defects, and allows the treated HfO<sub>2</sub> film holding good reliability as the gate dielectric.

Another important property of dielectric films is the reliability under gate bias stress. Due to the gate dielectric is stressed at a high field when the transistors are operating, so that it is demanded for gate dielectric to have excellent resistance to the impairment under long time stress at operating electric field. During high electric field stress, the carriers of leakage current and high electric field would impact the weak bonding, leading to more defects, higher leakage current and the degradation of transistor [46]. Therefore, the reliability of dielectric under gate bias stress would judge whether agrees with the application of gate dielectric. Figure 2-20 shows the variation of leakage current of different-treated HfO<sub>2</sub> films as a function of stress time at a high electric field = 5 MV/cm, where  $I_0$  is the initial leakage density. As well as the tendency of the measurement of breakdown voltage, the baking-treated HfO<sub>2</sub> film behaves the most rises in the degree of leakage current as the stress time increasing, because of the great amount of defects and weak bonding. However, after treating with 3000 psi-SCCO<sub>2</sub> process, the sputter-deposited HfO<sub>2</sub> film performs a fine reliability under high electric field stress, hence it is extremely suitable for the application of gate dielectric.

## 2.4 Summary

We have demonstrated experimentally the effects of low-temperature treatments on the dielectric characteristics of sputter-deposited HfO<sub>2</sub> film. The preliminary improvement in HfO<sub>2</sub> dielectrics is obtained by H<sub>2</sub>O vapor immersion at 150 °C, due to the deactivation of defects inside low-temperature deposited HfO<sub>2</sub> films and replacing these defects by the formation of Hf-O-Hf bonds. A further study also showed that the efficiency of passivating defects can be maximized via the SCCO<sub>2</sub> treatment which mixed with H<sub>2</sub>O and additive alcohol. Basing on the gas-like and high-pressure properties, the supercritical CO<sub>2</sub> fluids can affinity with H<sub>2</sub>O molecules

and infiltrate into  $\text{HfO}_2$  films to effectively deactivate these defects (or dangling bonds). After  $\text{SCCO}_2$  treatment, the amount of oxygen and the intensity of Hf-O-Hf bonds obviously rise, and the superior resistance to leakage current is gained as a result of the conduction mechanism transform into Schottky emission. The properties of  $\text{SCCO}_2$ -treated  $\text{HfO}_2$  film, such as larger dielectric constant, lower density of interface states, higher breakdown voltage of  $\text{HfO}_2$  film and excellent reliability under high electric field are presented in addition. These results indicate that the low-temperature  $\text{SCCO}_2$  fluids technology is greatly beneficial to enhance the dielectric properties of low-temperature deposited  $\text{HfO}_2$  films by reducing defects, and performs better electrical reliability.

