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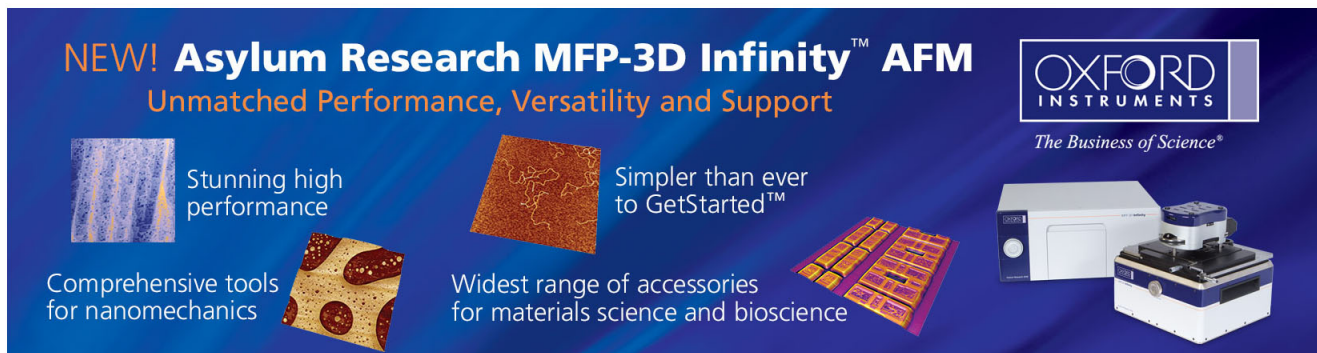Appl. Phys. Lett. **89**, 142907 (2006); 10.1063/1.2358841

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Low-temperature method for enhancing sputter-deposited HfO₂ films with complete oxidization

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A low-temperature method, supercritical CO_2 fluid (SCF) technology, is proposed to improve the dielectric properties of ultrathin hafnium oxide (HfO_2) film at 150 °C without significant formation of parasitic oxide at the interface between HfO_2 and Si substrate. In this research, the HfO_2 films were deposited by dc sputter at room temperature and post-treated by SCF which is mixed with 5 vol % propyl alcohol and 5 vol % H_2O. From high-resolution transmission electron microscopy image, the interfacial oxide of SCF-treated HfO_2 film is only 5 Å thick. Additionally, the enhancements in the qualities of sputter-deposited HfO_2 film after SCF process are exhibited by x-ray photoelectron spectroscopy and capacitance-voltage (C-V) measurement. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2753762]

In recent records, the high dielectric constant (high-k) materials, such as Al_2O_3, ZrO_2, and HfO_2, have been widely investigated and employed as gate dielectric of transistors. Due to the high-k materials hold thicker thickness than traditional gate dielectric, SiO_2, with similar capacitance, is effective for they avoid the significant direct tunneling current through the SiO_2.[1] Moreover, the high-k materials are applicable to the blocking oxide layer of nonvolatile memory for expediting the program/erase rate.[2] Many deposition methods have been used to prepare the high-k films.[3–5] The sputter deposition is more favorable among all these methods because of the advantages of simple process, high purity, low cost, and fitting to low-temperature fabrication that corresponds with the production of thin-film transistors. The high-temperature annealing is generally applied to improve the properties of sputter-deposited high-k films.[6–8] Nevertheless, the postannealing might cause the crystallization of HfO_2 film and the formation of parasitic oxide at the interface between HfO_2 and Si substrate. These phenomena will individually result in the unexpected leakage current via grain boundaries of HfO_2 film and the increase of equivalent oxide thickness.[7,8] In this investigation, for avoiding these phenomena as previous described, the supercritical CO_2 (SCCO₂) fluid technology is proposed to terminate traps in HfO_2 film

and enhance the performance of HfO_2 film at low temperature (150 °C). The supercritical fluid holds liquidlike property, giving them excellent capability to be a transporter. In addition, supercritical fluid has gaslike and high-pressure properties to efficiently diffuse into nanoscale structures without damage.[9,10] Therefore, it is allowed for supercritical fluid to carry H_2O molecules into thin HfO_2 films at low temperature and passivating the traps by H_2O molecules.[11,12]

The HfO_2 film layer was deposited on p-type (100) silicon wafers by reactive dc magnetron sputtering at room temperature under Ar/O_2 ambient, and the thicknesses of ultrathin HfO_2 films were measured to be about 8–10 nm by ellipsometer system. These wafers deposited with ultrathin HfO_2 films were split into three groups and treated by different methods for improving the properties of low-temperature deposited HfO_2 films. The first group, labeled as "baking-only treatment," was baked only on a hot plate at 150 °C for 2 h. The second group, labeled as "H_2O vapor treatment," was immersed into a pure H_2O vapor ambience at 150 °C for 2 h, in a pressure-proof stainless steel chamber. The third group, marked as "3000 psi SCCO₂ treatment," was placed in a supercritical fluid system at 150 °C for 2 h, where it was injected with 3000 psi SCCO₂ fluid that was mixed with 5 vol % propyl alcohol and 5 vol % pure H_2O. The propyl alcohol acts as surfactant between nonpolar-SCCO₂ fluid and polar-H_2O molecules, such that the H_2O molecules are uniformly distributed in SCCO₂ fluid and delivered into the

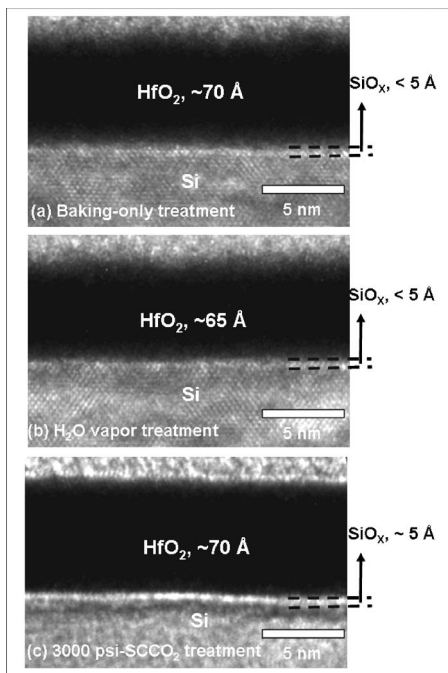[a]Author to whom correspondence should be addressed; electronic mail: tcchang@mail.phys.nsysu.edu.tw

FIG. 1. HRTEM images of HfO$_2$ films after (a) baking-only treatment, (b) H$_2$O vapor treatment, and (c) 3000 psi SCCO$_2$ treatment.

FIG. 2. XPS spectra of O$_{1s}$ energy levels of the HfO$_2$ films after different treatments.

HfO$_2$ film to passivate the traps. Afterward, the metal-insulator-semiconductor (MIS) capacitors were produced by thermally evaporating Al electrodes on the top surface of HfO$_2$ films and the back side of silicon wafer. The physical structure and chemical functional bonding of these treated-HfO$_2$ films were characterized by high-resolution transmission electron microscopy (HRTEM) and x-ray photoelectron spectroscopy (XPS). The electrical behaviors of HfO$_2$ films were analyzed from *C-V* measurements.

The HRTEM images of HfO$_2$ films with various post-treatments are shown in Fig. 1. For baking-treated and H$_2$O vapor-treated HfO$_2$ films, Figs. 1(a) and 1(b), there is only extremely thin oxide layer (<5 Å) between HfO$_2$ and Si substrates. The oxide layer could be explained reasonably by the formation of native oxide during depositing HfO$_2$. In Fig. 1(c), the slight increase of interfacial oxide is discovered after SCCO$_2$ process. This implies that the SCCO$_2$ fluid owns superior capability than H$_2$O vapor to operatively transport H$_2$O molecules into HfO$_2$ film, even arriving the interface and causing oxidization by H$_2$O molecules.[11,12] Although the thicker oxide layer (~5 Å) formed during SCCO$_2$ process, the parasitic oxide of SCCO$_2$-treated HfO$_2$ film remains evidently thinner than that of high-temperature annealing-treated HfO$_2$ film.[8] According to the prevention of parasitic oxide, the low-temperature treatment thereby is more suitable than the high-temperature process to enhance qualities of HfO$_2$ films.

To elucidate the variation in chemical bonding during processing HfO$_2$ films with different treatments, these treated-HfO$_2$ films were detected by XPS. Figure 2 displays the spectra of O$_{1s}$, and the energy state at about 530.3 eV is corresponding to Hf–O bonding.[13] Higher intensities and stronger binding energy of Hf–O bonding are observed in H$_2$O vapor-treated and SCCO$_2$-treated HfO$_2$ films, indicating that the H$_2$O molecules indeed can operatively react with the Hf dangling bonds (or traps) and form the stronger Hf–O bonding. Additionally, the excellent improvement in Hf–O
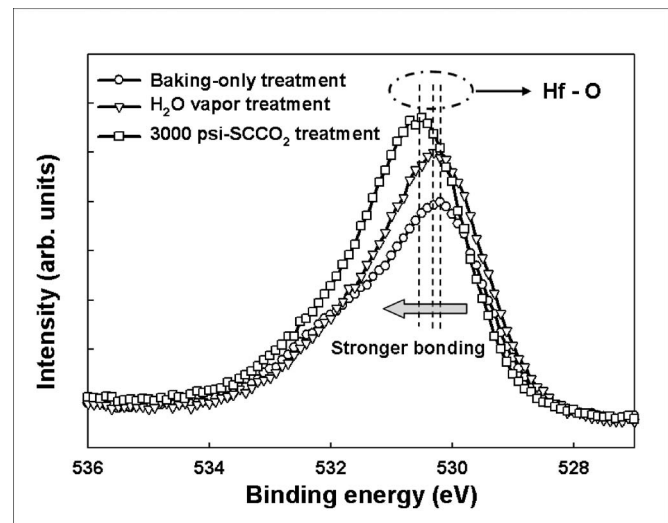
bonding is achieved with the SCCO$_2$ treatment, presenting that the H$_2$O molecules could be effectively diffused into HfO$_2$ films by SCCO$_2$ fluid, exactly as the tendency of HR-TEM results.

The *C-V* measurement is a common technology to recognize the qualities of dielectric films. Figure 3 plots the *C-V* characteristics of HfO$_2$ films, capacitor area of 5.43 × 10^{-3} cm^2, measuring under 1 MHz with gate bias swing from negative voltage to positive voltage (forward) and immediately from positive voltage to negative voltage (reverse). The slope of *C-V* curve in transient region, i.e., from C_{max} to C_{min}, is relative to the interface states.[14] The worst slope of *C-V* curve, expressing a large number of interface states exist, is performed by baking-treated HfO$_2$ film. With H$_2$O vapor treatment, the slope of *C-V* curve is sharper, and the effective dielectric constant (with the effect of interfacial oxide layer) is enhanced to 24.8. These could be explained by the reduction of traps at interface and in HfO$_2$ film. Furthermore, the optimum improvement is obtained after 3000 psi SCCO$_2$ process, and it indicates that the SCCO$_2$
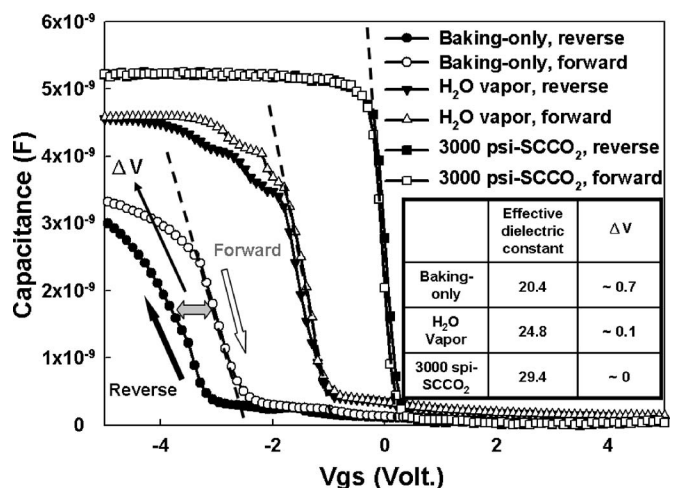

	Effective dielectric constant	ΔV
Baking-only	20.4	~ 0.7
H$_2$O Vapor	24.8	~ 0.1
3000 spi-SCCO$_2$	29.4	~ 0

FIG. 3. *C-V* characteristics of various-treated HfO$_2$ films with MIS capacitor area of 5.43 × 10^{-3} cm^2 and measuring frequency of 1 MHz. "Forward" means gate bias swing from negative voltage to positive voltage, and "Reverse" means the opposite swing direction. ΔV is the shifting value of *C-V* curve under forward and reverse gate bias swing.
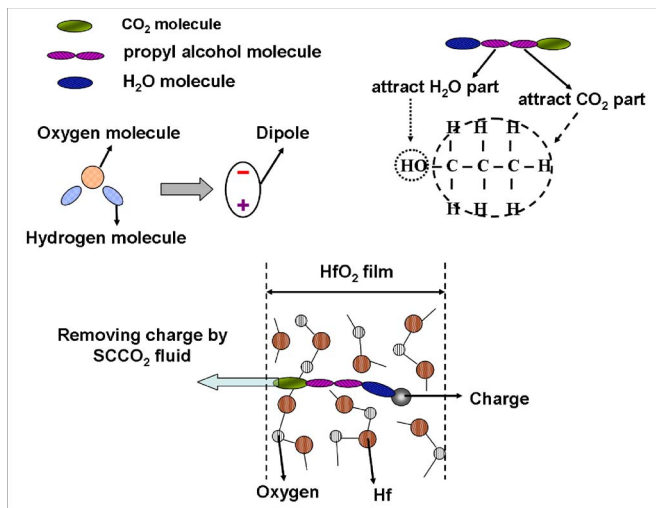
FIG. 4. (Color online) Mechanism for extracting fixed charges by $SCCO_2$ fluid which is mixed with 5 vol % propyl alcohol (connecting CO_2 and H_2O) and 5 vol % H_2O (taken as dipolar, connecting H_2O and fixed charge).

treatment possesses superior capability to passivate the traps, including both Hf dangling bonds and interface states.

Besides, in Fig. 3, the unfavorable shift of *C-V* curve under forward and reverse gate bias swing is observed in baking-treated and H_2O vapor-treated HfO_2 films, the shifting value of *C-V* curves (ΔV) is shown in the table of Fig. 3. This phenomenon is resulted from the existence of traps in HfO_2 films, which behave as carrier-trapping centers.[14,15] It evidently demonstrates that the baking-treated HfO_2 film keeps numerous traps because of the extensive ΔV, and these traps almost disappear after 3000 psi $SCCO_2$ treatment.

Another interesting event, form Fig. 3, is the movement of *C-V* curve after different treatments. Due to the work-function difference between Al ($\sim$4.3 V) and *p*-type Si substrate ($\sim$4.9 V) is about -0.6 V, the ideal position of transient region of *C-V* curve should occur near $V_{gs}=-0.6$ V. However, for baking-only treated HfO_2 film, the larger negative gate bias is required to reach transient region of *C-V* curve, and this is caused by the existence of positive charges (originated from the dc sputtering process) in HfO_2 film. After the 3000 psi $SCCO_2$ treatment, the *C-V* curve apparently moved to right. To explain this result, basing on Ref. 16, a possible mechanism to extract these positive charges with $SCCO_2$ fluid is proposed. As shown in Fig. 4, the polarized-H_2O molecule is taken as a dipole which attracts the charge in HfO_2 films. Afterward, the H_2O molecule and charge are connected with propyl alcohol and carried away by CO_2 molecule (or $SCCO_2$). For H_2O vapor-treated HfO_2 film, the portions of charges may remain in HfO_2 film due to the H_2O vapor owns poorer transport capability to remove charges and lead to the less shift of *C-V* curve.

In conclusion, the $SCCO_2$ fluid is developed as operative transporter to take the H_2O molecules into sputter-deposited HfO_2 films at 150 °C and terminate the traps in HfO_2 films by the oxidization with H_2O molecules. The apparent advancement of Hf–O bonding is verified experimentally, and only extremely thin parasitic oxide layer ($\sim$5 Å) appears between HfO_2 and Si substrate. Additionally, the superior *C-V* characteristic is also obtained after the $SCCO_2$ fluid process. These results evidence the improvements of $SCCO_2$ treatment in dielectric properties, including the rise of effective dielectric constant, reduction of interface states, and passivation of traps in HfO_2 film. Besides, the $SCCO_2$ fluid technology perhaps is an effective method to remove the charges in dielectric films.

[1] G. D. Wilk, R. M. Wallace, and J. M. Anthony, J. Appl. Phys. **89**, 5243 (2001).
[2] C. H. Lee, S. H. Hur, Y. C. Shin, J. H. Choi, D. G. Park, and K. Kim, Appl. Phys. Lett. **86**, 152908 (2005).
[3] K. Cherkaoui, A. Negara, S. McDonnell, G. Hughes, M. Modreanu, and P. K. Hurley, Proceedings of the IEEE 25th International Conference on Microelectronics, 2007, p. 351.
[4] Q. Fang, J. Y. Zhang, Z. M. Wang, J. X. Wu, B. J. O'Sullivan, P. K. Hurley, T. L. Leedham, H. Davies, M. A. Audier, C. Jimenez, J. P. Senateur, and I. W. Boyddefea, Thin Solid Films **427**, 391 (2003).
[5] M. Liu, Q. Fang, G. He, L. Q. Zhu, and L. D. Zhang, J. Appl. Phys. **101**, 034107 (2007).
[6] S. Jakschik, U. Schroeder, T. Hecht, M. Gutsche, H. Seidl, and J. W. Bartha, Thin Solid Films **425**, 216 (2003).
[7] B. H. Lee, L. Kang, W. J. Qi, R. Nieh, Y. Jeon, K. Onishi, and J. C. Lee, Tech. Dig. - Int. Electron Devices Meet. **1999**, 133.
[8] S. C. Chen, T. J. C. Lou, C. H. Chien, P. T. Liu, and T. C. Chang, Thin Solid Films **488**, 167 (2005).
[9] S. Ogawa, T. Nasuno, M. Egami, and A. Nakashima, Proceedings of the IEEE 2002 International Interconnect Technology Conference, 2002, p. 220.
[10] P. T. Liu, C. T. Tsai, T. C. Chang, K. T. Kin, and P. L. Chang, IEEE Trans. Nanotechnol. **6**, 29 (2007).
[11] T. Sameshima, K. Sakamoto, Y. Tsunoda, and T. Saitoh, Jpn. J. Appl. Phys., Part 2 **37**, L1452 (1998).
[12] M. Kunii, Jpn. J. Appl. Phys., Part 1 **45**, 660 (2006).
[13] Q. Fang, J. Y. Zhang, Z. Wang, M. Modreanu, B. J. O'Sullivan, P. K. Hurley, T. L. Leedham, D. Hywel, M. A. Audier, C. Jimenez, J. P. Senateur, and I. W. Boyd, Thin Solid Films **453-454**, 203 (2004).
[14] A. Koukab, A. Bath, and E. Losson, Solid-State Electron. **41**, 635 (1997).
[15] W. Y. Loh, B. J. Cho, M. S. Joo, M. F. Li, D. S. Chan, S. Mathew, and D. L. Kwong, Tech. Dig. - Int. Electron Devices Meet. **2003**, 927.
[16] T. Fukuda and H. Yanazawa, Jpn. J. Appl. Phys., Part 1 **43**, 936 (2004).