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

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A low-temperature method, supercritical CO₂ fluid (SCF) technology, is proposed to improve the dielectric properties of ultrathin hafnium oxide (HfO₂) film at 150 °C without significant formation of parasitic oxide at the interface between HfO₂ and Si substrate. In this research, the HfO₂ 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 % H₂O. From high-resolution transmission electron microscopy image, the interfacial oxide of SCF-treated HfO₂ film is only 5 Å thick. Additionally, the enhancements in the qualities of sputter-deposited HfO₂ 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 Al₂O₃, ZrO₂, and HfO₂, have been widely investigated and employed as gate dielectric of transistors. Due to the high-k materials hold thicker thickness than traditional gate dielectric, SiO₂, with similar capacitance, is effective for they avoid the significant direct tunneling current through the SiO₂. Moreover, the high-k materials are applicable to the blocking oxide layer of nonvolatile memory for expediting the program/erase rate. Many deposition methods have been used to prepare the high-k films. 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. Nevertheless, the postannealing might cause the crystallization of HfO₂ film and the formation of parasitic oxide at the interface between HfO₂ and Si substrate. These phenomena will individually result in the unexpected leakage current via grain boundaries of HfO₂ film and the increase of equivalent oxide thickness. In this investigation, for avoiding these phenomena as previous described, the supercritical CO₂ (SCCO₂) fluid technology is proposed to terminate traps in HfO₂ film and enhance the performance of HfO₂ 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. Therefore, it is allowed for supercritical fluid to carry H₂O molecules into thin HfO₂ films at low temperature and passivating the traps by H₂O molecules.

The HfO₂ film layer was deposited on p-type (100) silicon wafers by reactive dc magnetron sputtering at room temperature under Ar/O₂ ambient, and the thicknesses of ultrathin HfO₂ films were measured to be about 8–10 nm by ellipsometer system. These wafers deposited with ultrathin HfO₂ films were split into three groups and treated by different methods for improving the properties of low-temperature deposited HfO₂ 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 “H₂O vapor treatment,” was immersed into a pure H₂O 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 H₂O. The propyl alcohol acts as surfactant between nonpolar-SCCO₂ fluid and polar-H₂O molecules, such that the H₂O molecules are uniformly distributed in SCCO₂ fluid and delivered into the...
HfO₂ film to passivate the traps. Afterward, the metal-insulator-semiconductor (MIS) capacitors were produced by thermally evaporating Al electrodes on the top surface of HfO₂ films and the back side of silicon wafer. The physical structure and chemical functional bonding of these treated-HfO₂ films were characterized by high-resolution transmission electron microscopy (HRTEM) and x-ray photoelectron spectroscopy (XPS). The electrical behaviors of HfO₂ films were analyzed from C-V measurements.

The HRTEM images of HfO₂ films with various post-treatments are shown in Fig. 1. For baking-treated and H₂O vapor-treated HfO₂ films, Figs. 1(a) and 1(b), there is only extremely thin oxide layer (~5 Å) between HfO₂ and Si substrates. The oxide layer could be explained reasonably by the formation of native oxide during depositing HfO₂. In Fig. 1(c), the slight increase of interfacial oxide is discovered after SCCO₂ process. This implies that the SCCO₂ fluid owns superior capability than H₂O vapor to operatively transport H₂O molecules into HfO₂ film, even arriving the interface and causing oxidization by H₂O molecules. Although the thicker oxide layer (~5 Å) formed during SCCO₂ process, the parasitic oxide of SCCO₂-treated HfO₂ film remains evidently thinner than that of high-temperature annealing-treated HfO₂ film. According to the prevention of parasitic oxide, the low-temperature treatment thereby is more suitable than the high-temperature process to enhance qualities of HfO₂ films.

To elucidate the variation in chemical bonding during processing HfO₂ films with different treatments, these treated-HfO₂ films were detected by XPS. Figure 2 displays the spectra of O₁s, and the energy state at about 530.3 eV is corresponding to Hf–O bonding. Higher intensities and stronger binding energy of Hf–O bonding are observed in H₂O vapor-treated and SCCO₂-treated HfO₂ films, indicating that the H₂O 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 SCCO₂ treatment, presenting that the H₂O molecules could be effectively diffused into HfO₂ films by SCCO₂ fluid, exactly as the tendency of HRTEM results.

The C-V measurement is a common technology to recognize the qualities of dielectric films. Figure 3 plots the C-V characteristics of HfO₂ films, capacitor area of 5.43 × 10⁻³ cm², 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. The worst slope of C-V curve, expressing a large number of interface states exist, is performed by baking-treated HfO₂ film. With H₂O 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 HfO₂ film. Furthermore, the optimum improvement is obtained after 3000 psi SCCO₂ process, and it indicates that the SCCO₂...
After the 3000 psi SCCO2 treatment, the evidently demonstrates that the baking-treated HfO2 film the H2O vapor owns poorer transport capability to remove by CO2 molecule charge are connected with propyl alcohol and carried away keeps numerous traps because of the extensive function difference between Al charges and lead to the less shift of C-V curve. Afterward, the H2O molecule and traps almost disappear after 3000 psi SCCO2 treatment. However, for baking-only treated HfO2 film, the larger negative region of C-V curve should occur near \( V_{gs} = -0.6 \) V, the ideal position of \( C-V \) curve is shown in the table of Fig. 3. This phenomenon is resulted from the existence of traps in HfO2 films, which behave as carrier-trapping centers. It evidently demonstrates that the baking-treated HfO2 film keeps numerous traps because of the extensive \( \Delta V \), and these traps almost disappear after 3000 psi SCCO2 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 (\(-4.3 \) V) and p-type Si substrate (\(-4.9 \) 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 HfO2 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 HfO2 film. After the 3000 psi SCCO2 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 SCCO2 fluid is proposed. As shown in Fig. 4, the polarized-H2O molecule is taken as a dipole which attracts the charge in HfO2 films. Afterward, the H2O molecule and charge are connected with propyl alcohol and carried away by CO2 molecule (or SCCO2). For H2O vapor-treated HfO2 film, the portions of charges may remain in HfO2 film due to the H2O vapor owns poorer transport capability to remove charges and lead to the less shift of C-V curve.

In conclusion, the SCCO2 fluid is developed as operative transporter to take the H2O molecules into sputter-deposited HfO2 films at 150 °C and terminate the traps in HfO2 films by the oxidation with H2O molecules. The apparent advancement of Hf–O bonding is verified experimentally, and only extremely thin parasitic oxide layer (\(~5 \) Å) appears between HfO2 and Si substrate. Additionally, the superior C-V characteristic is also obtained after the SCCO2 fluid process. These results evidence the improvements of SCCO2 treatment in dielectric properties, including the rise of effective dielectric constant, reduction of interface states, and passivation of traps in HfO2 film. Besides, the SCCO2 fluid technology perhaps is an effective method to remove the charges in dielectric films.

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FIG. 4. (Color online) Mechanism for extracting fixed charges by SCCO2 fluid which is mixed with 5 vol % propyl alcohol (connecting CO2 and H2O) and 5 vol % H2O (taken as dipolar, connecting H2O and fixed charge).