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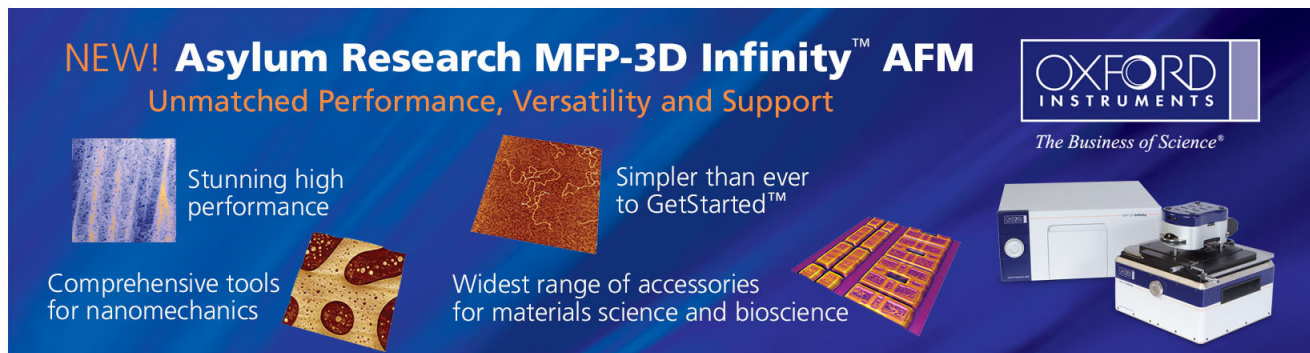
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Effects of supercritical CO₂ fluid on sputter-deposited hafnium oxide

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Low-temperature supercritical fluid (SCF) technology is employed to improve the dielectric characteristics of metal oxide film deposited at low temperature. In this investigation, hafnium oxide (HfO₂) film was sputter deposited at room temperature and post-treated with SCF at 150 °C, replacing typical high-temperature annealing process. From Fourier transformation infrared and thermal desorption spectroscopy measurement, the absorption peaks of Hf–O–Hf bonding and the oxygen content in HfO₂ film have, respectively, shown apparent raise. The leakage current density of the low-temperature deposited HfO₂ film is reduced significantly, and the conduction mechanism is modified from trap-assisted quantum tunneling to thermionic emission process, since SCF treatment effectively reduces the number of traps in HfO₂ film. © 2007 American Institute of Physics. [DOI: 10.1063/1.2743747]

Metal oxide dielectrics, such as Al₂O₃, Ta₂O₅, and HfO₂, have attracted much attention because of their potential application as memory cell capacitors and gate dielectrics in the ultralarge-scale-integration technology.^{1,2} Among several methods for producing metal oxide films,^{1–3} low-temperature technology is particularly appealing because it has a low thermal budget. Also, it is suitable for producing thin-film transistor liquid crystal displays that are based on glass substrates or plastics.^{4,5} However, dielectric films that are deposited at low temperature perform poorer properties and higher current leakage due to numerous traps present inside the metal oxide film.^{3,6,7} A post-treatment process must therefore be applied to low-temperature deposited metal oxide film to reduce electrical traps. High-temperature (>600 °C) annealing is traditionally performed to reduce the number of traps in metal oxide films.^{7–9} Nevertheless, high-temperature annealing raises several issues. For instance, crystallization may occur during the process, producing an unexpected leakage current through grain boundaries.^{9–11} Moreover, the high-temperature process is not applicable to the substrates with low glass transition temperatures (T_g), such as glasses and plastics.¹² Accordingly, a technology for trap passivation at low temperature must be developed to extend the applications of metal oxide dielectrics. In this work, a supercritical CO₂ (SCCO₂) fluid process at 150 °C is proposed to enhance the low-temperature deposited HfO₂ films. The supercritical fluid exhibits liquidlike property, giving them excellent transport capacity. Also, supercritical fluid has gaslike properties and efficiently diffuse into nanoscale structures without damage.^{13–16} Hence, these advantages are adequately employed to passivate the traps in metal oxide dielectric films at low temperature.

In this experiment, the HfO₂ film layer was deposited on p-type (100) silicon wafers by reactive dc magnetron sputtering at room temperature under Ar/O₂ ambient. The thickness of as-deposited HfO₂ films was 10 nm, as measured by an ellipsometer system. Subsequently, these wafers with 10-nm-thick HfO₂ film were split into three groups, and processed by different post-treatments to improve the properties of low-temperature deposited HfO₂ film. The first group labeled as *Baking-only treatment*, was the control sample, and 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 *SCCO₂ treatment*, was placed in a supercritical fluid system at 150 °C for 2 h, where 3000 psi of SCCO₂ fluid that were mixed with 5 vol % of propyl alcohol and 5 vol % of pure H₂O were injected. 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. Following these different treatments, the thickness of the HfO₂ films is almost unchanged, as checked by the identical ellipsometer system. Fourier transformation infrared spectroscopy (FTIR) and thermal desorption spectroscopy (TDS) were also used to investigate the evolution of chemical functional bonding and the amount of oxygen in HfO₂ films, respectively. Electrical measurements were made on metal insulator semiconductor (MIS) capacitors which were produced by thermally evaporating Al electrodes on the top surface of the HfO₂ films and the back side of the silicon wafer.

Figure 1 shows FTIR spectra of HfO₂ films after various post-treatments. The functional groups at 509 and 690 cm⁻¹ are associated with Hf–O–Hf bonding,¹⁷ and the absorption peak at around 1070 cm⁻¹ corresponds to the Si–O–Si bond.

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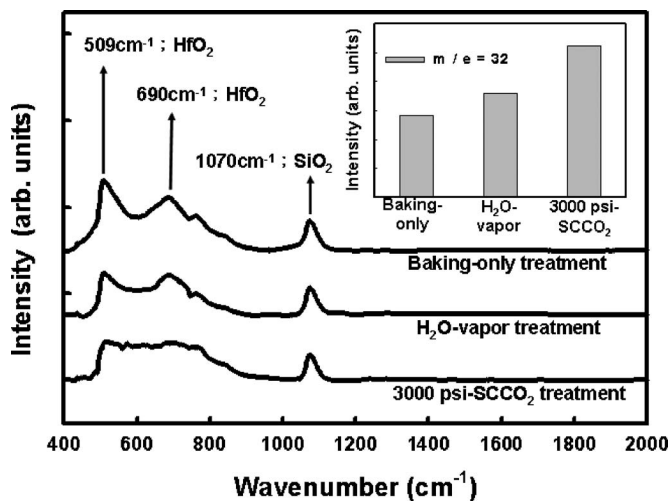


FIG. 1. FTIR spectra of sputter-deposited HfO₂ films after various low-temperature (150 °C) treatments. The inset corresponds the sum of m/e (mass-to-charge ratio)=32 peak, which is attributed to O₂, of TDS analysis.

The Si–O–Si bond originates from the formation of the interface layer (SiO_x) between HfO₂ film and silicon wafer during fabrication of HfO₂ films in Ar/O₂ ambient. The peak intensities of Si–O–Si bond after different treatments are almost similar, indicating that these post-treatments do not differently affect the thickness and quality of the interfacial SiO_x film. However, the peak intensity of Hf–O–Hf bands of the H₂O vapor treated HfO₂ film exceeds that of the baking-only treated HfO₂ film. The H₂O vapor is thus believed to permeate the HfO₂ film and reacts with Hf dangling bonds (or traps) to form Hf–O–Hf bands. These traps in the sputter-deposited HfO₂ film can thereby be passivated by H₂O vapor molecules. Furthermore, SCCO₂ treatment conspicuously increases the intensity of Hf–O–Hf bonding peaks in FTIR, suggesting that the transport efficiency of H₂O molecules into HfO₂ films is maximized by SCCO₂ fluid, and potentially modifying the dielectric characteristics of HfO₂ film. The TDS measurements, as shown in the inset, were made out upon heating these treated HfO₂ films from 50 to 800 °C at a heating rate of 10 °C/min in vacuum (10⁻⁵ Pa). In the TDS analysis, an m/e (mass-to-charge ratio)=32 peak, attributed to O₂, is monitored to evaluate the amount of oxygen outgassing from HfO₂ films. Clearly, the oxygen content is highest in the SCCO₂-treated HfO₂ film, the result of which is certainly consistent with the FTIR observations.

The leakage current densities of the variously treated HfO₂ films are shown as a function of applied electric field in Fig. 2. The baking-only treated HfO₂ film exhibits the greatest leakage current among the variously treated films, because it has poor dielectric characteristics with numerous traps inside the HfO₂ film.^{3,6,7} The improvement of electrical characteristics is first observed by using a H₂O vapor process, indicating that the H₂O vapor alters dielectric properties of the low-temperature deposited HfO₂ film. However, a high leakage current density still appears at larger applied electric field and may be reasonably inferred to depend on the defect passivation efficiency. The SCCO₂-treated HfO₂ film exhibits the lowest leakage current density, about 2×10^{-7} A/cm² even biased at an electric field of 3 MV/cm. This proves that SCCO₂ treatment is the most effective method to improve electrical characteristics of the sputter-deposited HfO₂ film in this work. The electrical performance

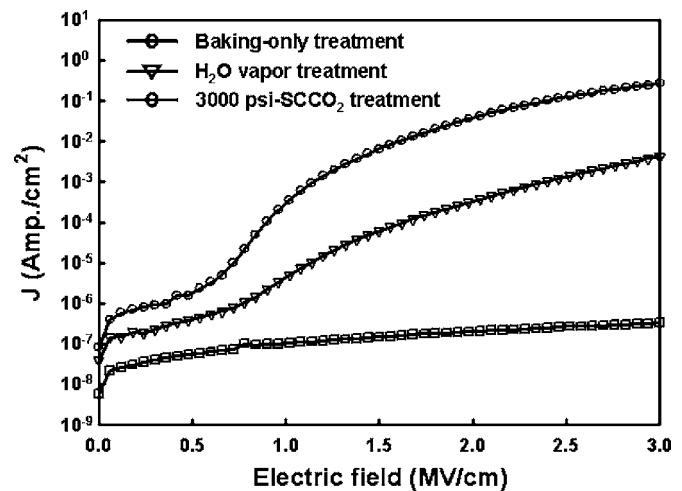


FIG. 2. Leakage current densities (J) of sputter-deposited HfO₂ films after different low-temperature treatments as a function of the applied electric field (E). (The negative bias is applied on gate electrode.)

is also consistent with the FTIR analysis, which reveals that SCCO₂ treatment effectively enhances the dielectric properties of HfO₂ film.

The leakage conduction mechanism is also investigated to support the comments above about electrical improvement of HfO₂ film. Figure 3(a) plots $\ln(J/E)$ versus the reciprocal of electric field ($1/E$) for the baking-only treated HfO₂ film and the inset present a schematic energy band diagram which elucidates the leakage transport mechanism. A good linear fit explains that the Fowler-Nordheim tunneling¹⁸ occurs as the electric fields stronger than 0.7 MV/cm, which may be attributed to the trap-assisted tunneling because the baking-only treated HfO₂ film contains numerous traps,¹⁹ as shown in the inset in Fig. 3(a). A plot of the leakage current density of the SCCO₂-treated HfO₂ film versus the square root of the applied electric field gives useful information on the leakage behavior, as shown in Fig. 3(b). The leakage current density of the SCCO₂-treated HfO₂ film is linearly related to the square root of the applied electric field, indicating Schottky-Richardson emission transport mechanism.²⁰ Schottky-type conduction can be verified by comparing the theoretical value of $\beta_{SE} (=e^3/4\pi\epsilon_0\epsilon)^{1/2}$ with the calculated value obtained from the slope of the experimental curve $\log J$ as a function of $E^{1/2}$,²¹ where e is the electronic charge, ϵ_0 is the permittivity of free space, and ϵ is the relative dielectric constant. The Schottky emission induced by the thermionic effect is caused by electron transport across the potential energy barrier via field-assisted lowering at the metal-insulator interface, as shown in the inset of Fig. 3(b) and it is independent of traps. The evolution of conduction mechanisms from trap-assisted tunneling to Schottky emission can confirm the minimization of the number of these traps inside low-temperature deposited HfO₂ film by implementing the proposed SCCO₂ technology.

The effects of low-temperature treatments on the dielectric characteristics of the sputter-deposited HfO₂ film were demonstrated experimentally. The preliminary improvement in the HfO₂ dielectrics was obtained by H₂O vapor immersion at 150 °C, and was associated with the enhancement of Hf–O–Hf bonds. A further study also demonstrated that SCCO₂ treatment with additive alcohol maximizes trap passivation efficiency. The supercritical CO₂ fluid has an affinity

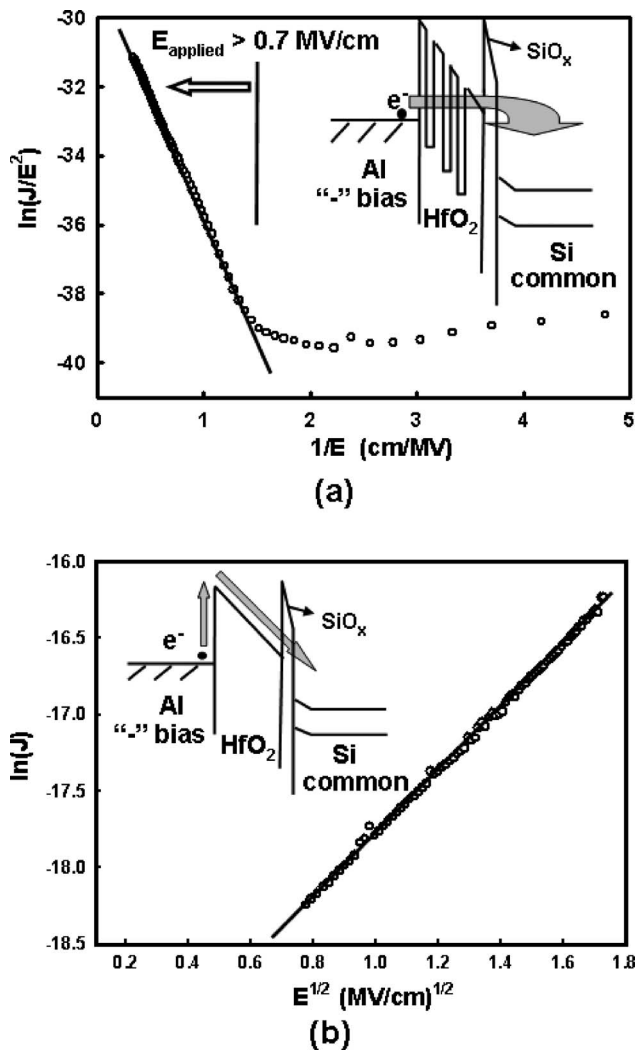


FIG. 3. (a) Curve of $\ln(J/E)$ of the baking-only treated HfO_2 vs reciprocal of electric field ($1/E$), and a schematic energy band diagram accounting for trap-assisted tunneling is shown in the inset. (E_{applied} is the electric field applied on the gate electrode of MIS capacitor.) (b) Leakage current density of SCCO_2 -treated HfO_2 vs the square root of electric field ($E^{1/2}$). The inset shows the energy band diagram of Schottky-type conduction mechanism.

for H_2O molecules and exhibits the gaslike properties to infiltrate into HfO_2 thin film, such that it is allowed for SCCO_2 to effectively deactivate the traps (or dangling bonds) inside low-temperature deposited HfO_2 films. Both material analy-

sis and the study of electrical mechanism also support the inferences in this investigation. These results indicate that the low-temperature SCCO_2 fluid technology is greatly beneficial to enhance the dielectric properties of sputter-deposited HfO_2 films by passivating traps, improving superior electrical reliability.

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