Dielectric relaxation of atomic-layer-deposited HfO₂ thin films from 1 kHz to 5 GHz

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The dielectric relaxation of HfO₂ thin films grown by atomic-layer deposition (ALD) was studied as a function of frequency from 1 kHz to 5 GHz. The dielectric relaxation of the ALD HfO₂ films followed a power-law dependence known as the Curie–von Schweidler relaxation law both in the kHz and GHz ranges, and the relaxation exponents were consistent with the measured dielectric losses. The behavior of the dielectric response for the HfO₂ thin films may be attributed to defect sites in the HfO₂ layer and/or interface. © 2005 American Institute of Physics.

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The search for suitable candidates to replace SiO₂ (or SiO₂–Nₓ) as the gate dielectric in future complementary metal-oxide-semiconductor (CMOS) devices has recently received enormous attention, since conventional SiO₂-based gate oxides have approached their thickness limit of scaling. Among many potential high-k oxides, one of the most promising candidates is hafnium oxide (HfO₂), due to its high dielectric constants, thermodynamic compatibility of the interface with Si, gate polycrystalline silicon compatibility, and relatively large band gap. In particular, HfO₂ gate dielectrics grown by atomic layer deposition (ALD) have been studied extensively, and demonstrated encouraging electrical performance, with good uniformity and conformality.

The dielectric relaxation of ALD HfO₂ thin films has not been studied up to the GHz range, even though the effect of dielectric relaxation can influence the performance of metal-oxide-semiconductor (MOS) devices with high-k gate oxides. The dielectric loss due to the dielectric relaxation can deteriorate the performance of MOS field effect transistors. Reisinger et al. reported that the dielectric relaxation is larger for most high-k dielectrics than for SiO₂. Moreover, it is important to accurately characterize the dielectric relaxation of HfO₂ thin films up to the GHz region due to the operating frequency range of complementary MOS. In this letter, the behavior of the dielectric constants and the losses for ALD HfO₂ thin films were studied as a function of frequency from 1 kHz to 5 GHz, for the first time.

The HfO₂ thin films with an approximately 10 nm thickness were deposited on a heavily phosphorous-doped Si substrate (ρ ≈ 10⁴ Ω cm) in a traveling-wave-type ALD reactor (Evertek Plus 200™). Before deposition, the substrates were treated with a dilute HF solution to remove the native oxides. The Hf source and the oxidant were tetrakis(ethylmethylamino)hinium liquid precursors and H₂O₂, respectively, and the deposition temperature was 300 °C. The as-deposited samples were annealed in N₂ and O₂ ambient at 500 °C for 5 min in a rapid thermal anneal chamber. A Au top electrode (100 nm) was deposited on ALD HfO₂/phosphorous-doped Si to measure the dielectric properties, using the metal-insulator-metal (MIM) and circular-patch capacitor structures, respectively, in the low frequency (~kHz) and in the microwave (~GHz) ranges. A phosphorous-doped Si substrate (without a separate metal bottom electrodes) was used to maintain a similar interface with HfO₂/Si. The dielectric losses and constants of the Au/HfO₂/phosphorous-doped Si (MIM) capacitors were measured using an impedance analyzer (HP 4194A) and a vector network analyzer (HP 8510C), respectively, in the 1 kHz–10 MHz and 0.1–5 GHz range. In the case of high-frequency measurements, the parasitic effects from the resistance in the bottom/top electrode and contact were removed by developing an equivalent-circuit model.

The metal-insulator-semiconductor (MIS) capacitors were fabricated by depositing Pt top electrodes (120 nm) on ALD HfO₂/Si (ρ ≈ 10⁴ Ω cm). Both the MIS and MIM capacitors were annealed at 400 °C for 30 min under a forming gas (4% H₂/N₂). The capacitance-voltage (C-V) characteristics of the Pt/HfO₂/Si (MIS) capacitors were measured using an impedance analyzer (HP 4194A). Thickness and microstructures were analyzed by high-resolution transmission electron microscopy [(HRTEM) JEM-3000F], and chemical-bond states were analyzed by x-ray photoelectron spectroscopy (XPS).

Figure 1 shows the HRTEM cross-section images of the as-deposited and postannealed samples at 500 °C in N₂ and O₂. The as-deposited HfO₂ films show an amorphous HfO₂ layer (~10 nm thick), and an underlying thin amorphous interfacial layer (IL) formed on the Si substrate during deposition. N₂ annealing results in crystallization and densification of the HfO₂ layer, and to an increase in the IL thickness. Similar effects are observed for O₂ annealing, where a thicker IL than N₂ annealing is observed.

The dielectric constants (ε) and dielectric losses (tan δ) of the as-deposited and annealed HfO₂ films are shown in Fig. 2, as a function of frequency ranging from 1 kHz to 5 GHz. The data for 1 kHz–10 MHz and
0.1–5 GHz were obtained from the impedance and the network analyzers, respectively, and the gap is due to the change in the measurement techniques. The frequency dependence of the dielectric losses between 50 kHz and 10 MHz is caused by uncompensated parasitic effects. At 2 GHz, the dielectric constants of the as-deposited HfO₂ films are ~15, and that of the annealed samples in N₂ and O₂ are ~13 and ~12, respectively. The decrease in the dielectric constants for the postannealed samples is attributed to an increase in the IL thickness (as shown in Fig. 1).

The dielectric constants of the ALD HfO₂ thin films clearly show a power-law dependence known as the Curie–von Schweidler law \( (\varepsilon \approx f^{n-1}) \), where the value of the exponent \( n \) indicates the degree of dielectric relaxation. The dielectric losses can be also obtained by the degree of relaxation in the dielectric constants \( [\tan \delta = \cot(n\pi/2)] \). This relaxation is expected by the hopping of electric charges between localized sites, which originate from impurities, defects, disorder (Anderson localization), electron-phonon coupling (polarons), etc. However, the origin of the various localized charge carriers in the ALD HfO₂ thin films needs to be elucidated.

Figure 3 shows the measured dielectric losses and the values of \( n \) obtained from the least-square fit \( (\varepsilon \approx f^{n-1}) \). The dielectric losses (averaged at 2–50 kHz and 0.1–2 GHz, respectively), are 0.013±0.002 and 0.013±0.002 for the as-deposited samples. These losses are reduced to 0.010±0.002 and 0.008±0.002 by N₂ annealing and to 0.007±0.002 and 0.005±0.002 by O₂ annealing. The exponent \( n \) in the 2–50 kHz range also depends on the annealing conditions, being 0.9957±0.0001 for the as-deposited samples, and increases to 0.9960±0.0001 and 0.9971±0.0002, respectively, for the samples annealed in N₂ and O₂. The values of \( n \) for 0.1–2 GHz were found to have a similar tendency. Moreover, the relaxation exponents were consistent with the measured dielectric losses. The decrease in the dielectric losses and the increase in the exponent \( n \) with postannealing may correlate with the reduction in the localized defect sites in the HfO₂ layer.

To characterize the defects in the HfO₂ films, the counterclockwise hysteresis and interface-trap densities were extracted from the C–V curves. Figure 4 shows these values at 1 MHz (Pt/HfO₂/Si) for the as-deposited films and those annealed in N₂ and O₂. The hysteresis of the C–V curves is believed to be due to the charge trapping under a negative bias. The reduction in hysteresis (~60 and ~10 mV for N₂ and O₂ annealing, respectively) indicates that the densities of the carrier-trapping defects decreased as a result of annealing. The interface-trap density obtained from the C–V using
the Terman method is approximately $1.1 \times 10^{12}$ cm$^{-2}$ eV$^{-1}$ for the as-deposited HfO$_2$ films, and reduces to $8.4 \times 10^{11}$ and $7.5 \times 10^{11}$ cm$^{-2}$ eV$^{-1}$ for the annealed samples in N$_2$ and O$_2$, respectively, which suggests that the extent of Hf–O–Si bond formation.\textsuperscript{17,18} The shoulder peak at $\sim$532 eV attributed to interfacial O atoms in nonstoichiometric HfSiO$_x$ also behaves in a similar manner.\textsuperscript{17} In Fig. 5(b), the Hf 4$f_{5/2}$ and Hf 4$f_{7/2}$ peaks attributed to Hf–O bond formation also shift to a higher binding energy by N$_2$ and O$_2$ annealing. In our films, the peak shifts to a higher energy are possibly due to both the formation of Hf–O–Si bonds and the enhanced charge-transfer effects as a result of the oxidation of HfO$_2$.\textsuperscript{19}

The HfO$_2$ thin films grown by the ALD process clearly exhibited the frequency dispersion due to dielectric relaxation. Postannealing reduced the dielectric losses and frequency dispersion, while the growth of IL during annealing decreased the dielectric constants of the HfO$_2$ films. Therefore, the appropriate annealing conditions of the HfO$_2$ gate dielectric are essential to find the optimal compromise between a thin IL (with a minimal reduction of dielectric constants) and a high-quality film (with low dielectric losses).

In conclusion, the dielectric constants and losses of the ALD HfO$_2$ thin films grown by ALD were effectively measured up to the GHz ranges. The dielectric relaxation of the ALD HfO$_2$ films followed a power-law dependence from 1 kHz to 5 GHz, and the relaxation exponent was consistent with the measured dielectric losses. The behavior of the dielectric response for the ALD HfO$_2$ thin films may be due to various defects in the HfO$_2$ layer and/or interface. Further studies are needed to determine the exact relaxation mechanisms in the ALD HfO$_2$ thin films.

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\textsuperscript{11}S. Ramathran, C. M. Park, and P. C. McIntyre, Appl. Phys. Lett. 91, 4521 (2002).