Electrical and dielectric properties of Hafnium oxide Hfo2-A Review

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Abstract:

Hafnium oxide (HfO_2) has been widely studied for its dielectric properties, especially in memory devices. This review focuses on its electrical and di-electrical properties. The scaling of metal-oxide-semiconductor transistors has led to the silicon dioxide layer, being so thin that its leakage current increases exponentially. Consequently, the SiO_2 has been reported to be replaced with a physically thicker layer of oxides of higher dielectric constant (k) or 'high-k' gate oxides such as HfO_2 and Al_2O_3. The electrical parameters such as dielectric constant, flat-band shift, and interface trap density can be determined through CV measurement. The low leakage current density can be obtained from IV measurement. We will look into these properties and explore the suitability of these high k-based MOS capacitors for advanced CMOS technologies.

Introduction:

Over recent decades, computing has advanced through transistor miniaturization, with flash memory as the dominant form of non-volatile memory (NVM). To enhance scalability, high-k oxide materials, including sub-stoichiometric hafnium oxide (HfO_x) and stoichiometric hafnium oxide (HfO_2), have been adopted. HfO_2 is particularly attractive due to its high dielectric constant (20–25) and wide bandgap (5.3–5.7 eV), offering advantages over traditional SiO_2. The discovery of ferroelectricity in 10-nm doped HfO_2 thin films has opened new possibilities for ferroelectric memory and advanced electronics. Unlike traditional ferroelectric materials like PZT and BTO, HfO_2 maintains and even enhances ferroelectric properties at the nanoscale, making it ideal for miniaturized devices. Its advantages, including a wide bandgap (~5.5 eV), high dielectric constant, extreme thinness, and compatibility with CMOS technology, have spurred research into its use in applications such as ferroelectric memory, Fe-FETs, energy harvesters, and pyroelectric sensors. The HfO_2-based ferroelectric memory is not only an ideal memory with clear advantages such as nonvolatility, low power consumption, high endurance, and high-speed writing, but is also the most suitable for memory device embedded applications [1].

The as-deposited layers of high-k materials like HfO_2 show large negative fixed charges, interface state densities, and charge trapping compared to SiO_2. These issues can be mitigated by introducing an intermediate oxide layer or post-deposition high-temperature processes. In this study, HfO2 thin films are sputtered onto p-Si (100) substrates, and their structural, chemical, surface topography, and electrical properties are analysed using X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, and semiconductor characterization systems [2]. HfO2 thin films have been deposited using many deposition techniques, such as atomic layer deposition (ALD), metal-organic chemical vapour deposition (MOCVD), and sputtering. Among the many deposition methods, ALD is extensively used for HfO2 thin film deposition. The ALD is a novel semiconductor thin film deposition technology, which controls the surface reaction of the precursor on the substrate. The ALD process can find its advantages in accurate thickness control and excellent step coverage because the growth rate only depends on the number of growth cycles and the lattice parameters of materials [2].

Experiment:

<u>Sputtering deposition of HfO2:</u>

The deposition of HfO2 using sputtering is one of the fundamental deposition techniques used to deposit thin films on semiconductor surfaces. The native oxide is removed or etched from the layer of the semiconductor material using Hf to get a pristine Si surface. The cleaned substrate is put into a vacuum chamber to avoid contamination and controlled deposition. High purity HfO2 is placed into the chamber along with argon gas, a potential difference is applied across the chamber to accelerate the Ar+ ions towards the target. The sputtered HfO2 atoms travel through the vacuum chamber and condense onto the Si substrate, forming a thin film. The thickness of the film can be controlled by adjusting deposition parameters such as power, gas pressure, and time.

<u>Atomic layer deposition:</u>

Among the many deposition methods, ALD is extensively used for HfO2 thin film deposition. The ALD is a novel semiconductor thin film deposition technology, which controls the surface reaction of the precursor on the substrate. The ALD process can find its advantages in accurate thickness control and excellent step coverage because the growth rate only depends on the number of growth cycles and the lattice parameters of materials [3].

After deposition, the HfO2 film is analysed using various techniques to assess its properties:

The thickness of the HfO2 thin film was measured using ellipsometry. The chemical compositions of the HfO2/Hf thin films were investigated using AES (auger electron spectroscopy). Microstructures of the thin films were investigated by XRD (X-ray diffractometry). The analysis of the interfacial region of HfO2/Si was done using XPS (X-ray photoelectron spectrometry) and TEM (transmission electron microscopy). The C-V analysis of the MOS capacitors was based on conventional MOS C-V theory. The C-V measurements were achieved by using a 1 MHz C meter. The IV measurements were performed using a semiconductor parameter analyser [3].

After the deposition of HfO2 is completed on the Si substrate, the obtained device is annealed at high temperatures in presence of oxygen or forming gas to treat the defects, improve the electric properties, and reduce impurities and stress.

Result and discussion:

<u>Ellipsometer:</u>

The thickness and refractive index of HfO2 thin films, grown at different deposition times, were measured using a spectroscopic ellipsometer at a 70-degree angle. The results show that as the sputtering deposition time increases, the film thickness also increases. The refractive index values range from 1.90 to 1.99, with only minor variations observed as the deposition time changes. These measured refractive index values align well with the expected refractive index of HfO2, as shown in Fig. 1.[2]

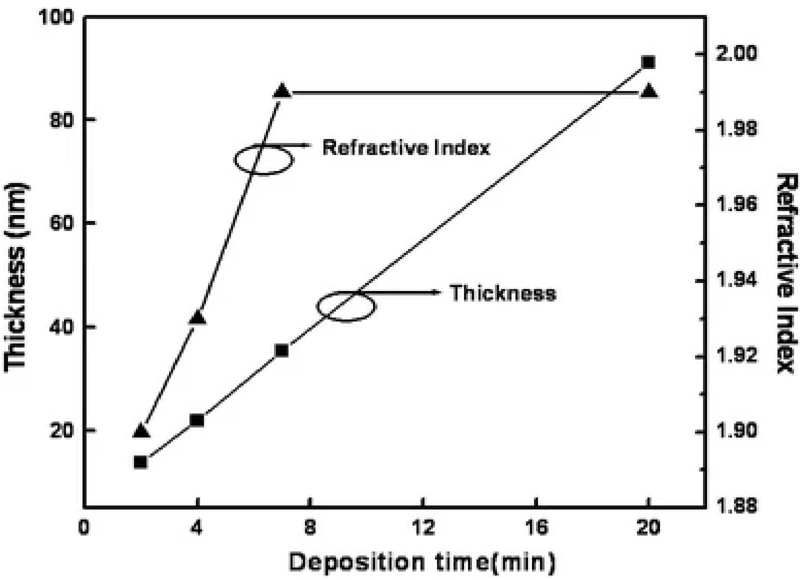

Fig. 1 Thickness and refractive index as function of deposition time.

XRD:

The crystal structure of HfO2 thin films was studied using X-ray diffraction (XRD) measurements, with the diffraction patterns displayed in Fig. 2. The measurements were conducted using a BRUKER XRD system with a Cu Kα radiation source (wavelength: 1.5402 Å). The peaks in the XRD patterns were matched with the ICDD database to identify the crystallographic phases based on their 2θ values and relative intensities. It was found that the crystallization of HfO2 films depends on factors such as growth temperature, film thickness, and the type of underlying layer. In this study, the HfO2 thin films were confirmed to be in the monoclinic phase, consistent with ICDD card no. 34-0104.[2]

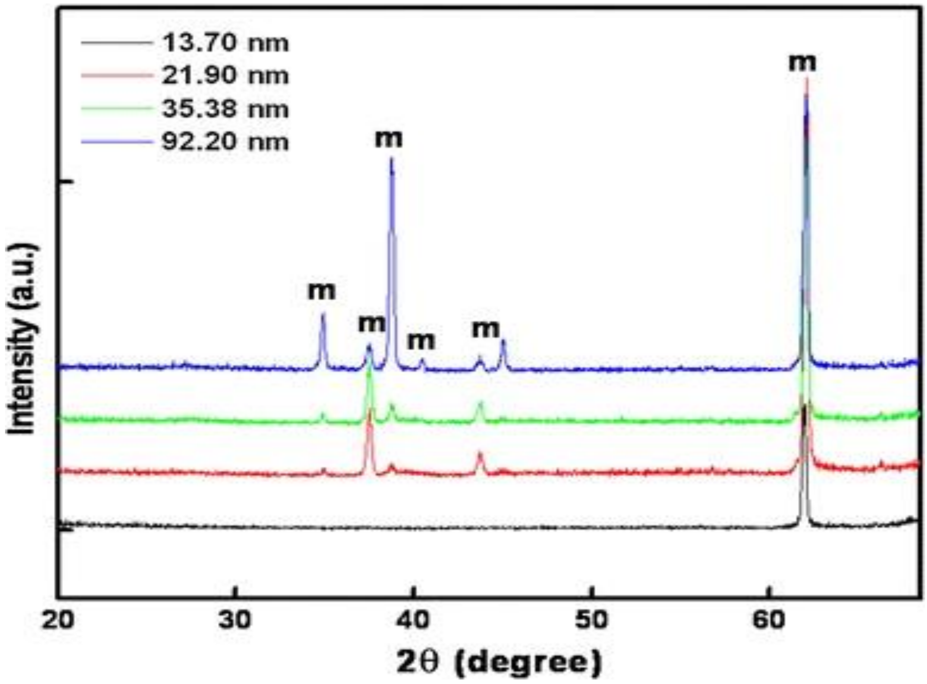

Fig. 2 XRD pattern of the deposited HfO2 films.

Capacitance–voltage and conductance–voltage measurement:

Figure 4, presents a typical high-frequency (1 MHz) capacitance-voltage (C–V) curve for a sample with varying physical thicknesses of HfO2 gate insulator thin films. The results show that as the thickness of the HfO2 film increases, the capacitance in the accumulation region decreases, which aligns with the behaviour predicted by the parallel plate model of a metal-oxide-semiconductor (MOS) capacitor. This is consistent with the relationship between capacitance and thickness in MOS capacitors, where increased thickness results in reduced capacitance.[2]

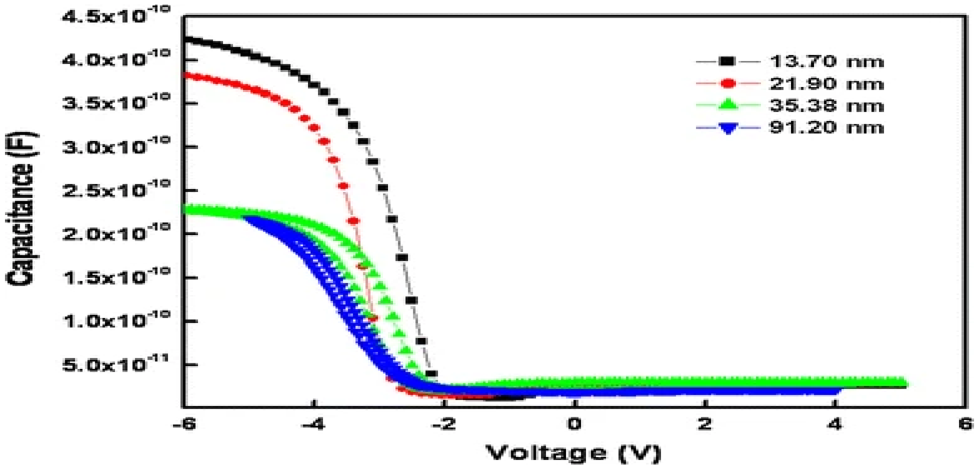

Fig. 4 Capacitance–voltage curve for different values of physical thickness.

Figure 5, displays high-frequency (1 MHz, 500 kHz, and 10 kHz) capacitance-voltage (C–V) curves for a HfO2 thin film sample with a thickness of 35.38 nm. The inset shows the conductance-voltage (G–V) measurement. From the maximum capacitance in the accumulation region, the effective dielectric constant (k-eff) of the film is calculated to be 7.99. The total capacitance is modelled as the series combination of the capacitances of the interfacial SiO2 layer and the HfO2 layer, satisfying the formula:

$1/C = 1/C_{SiO2} + 1/C_{HfO2}$

where $CSiO2$ and $CHfO2$ are the capacitances of the SiO2 and HfO2 layers, respectively. The C–V curves show minimal frequency dispersion in the accumulation region between 10 kHz and 1 MHz, which may be due to the series resistance in the MOS device structure.[2]

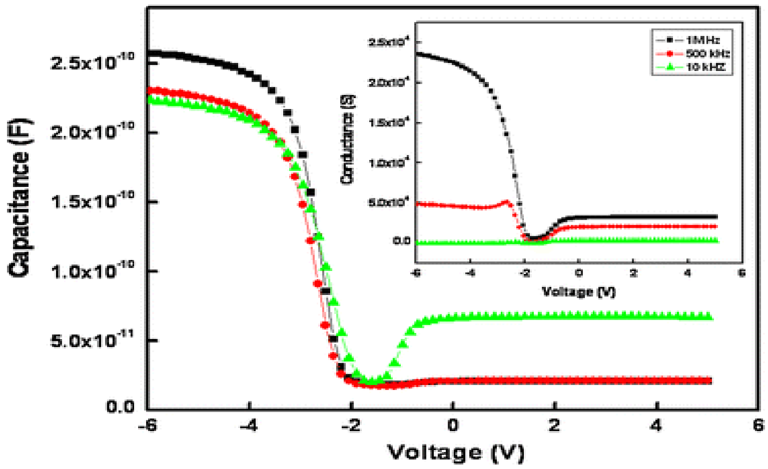

Fig. 5 C–V and G–V (inset) curves for different values of measurement frequency

At low frequencies, interface dangling bonds become significant due to their slow response times, which affect the C–V characteristics. Specifically, the flat-band voltage shifts in the positive direction as the frequency decreases. In Fig. 4, it is observed that the C–V curves for HfO2 films with thicknesses of 35.38 nm and 91.20 nm measured during increasing and decreasing gate bias voltages coincide well, indicating minimal hysteresis in the bidirectional C–V characteristics. This suggests that the sample has a low oxide charge density. The effective oxide charges (*Qeff)* are calculated for the 1 MHz measurement frequency using a specific equation, likely related to capacitance and flat-band voltage shift.

Q-eff = delta (V_{FB})*Cox/(q*A)

The oxide-semiconductor interface trap densities (*DitD_{it}*Dit) for the investigated HfO2 samples were estimated using high-frequency (1 MHz) C–V and G–V measurements, as shown in the inset of Fig. 5. The estimation was performed using the conductance technique and the following equation:

$$D_{it} = \frac{2}{qA} \cdot \frac{G_{m,\max}/x}{\left(\frac{G_{m,\max}}{xC_{ox}}\right)^2 + \left(\frac{C_m}{C_{ox}}\right)^2}$$

Where, C_{ox} is the oxide capacitance, $G_{m,\ max}$ is the maximum conductance, Cm is the capacitance of the metal, q is the electronic charge, A is the electrode area and x is the frequency(rad/sec).

Leakage current behaviour:

The leakage current density behaviour of fabricated MOS structure is obtained from the I–V measurement. Typical J– V characteristics of the HfO2 films are shown in Fig. 6. A well-behaved I–V curve is obtained for positive voltage with a step of 0.3 V.

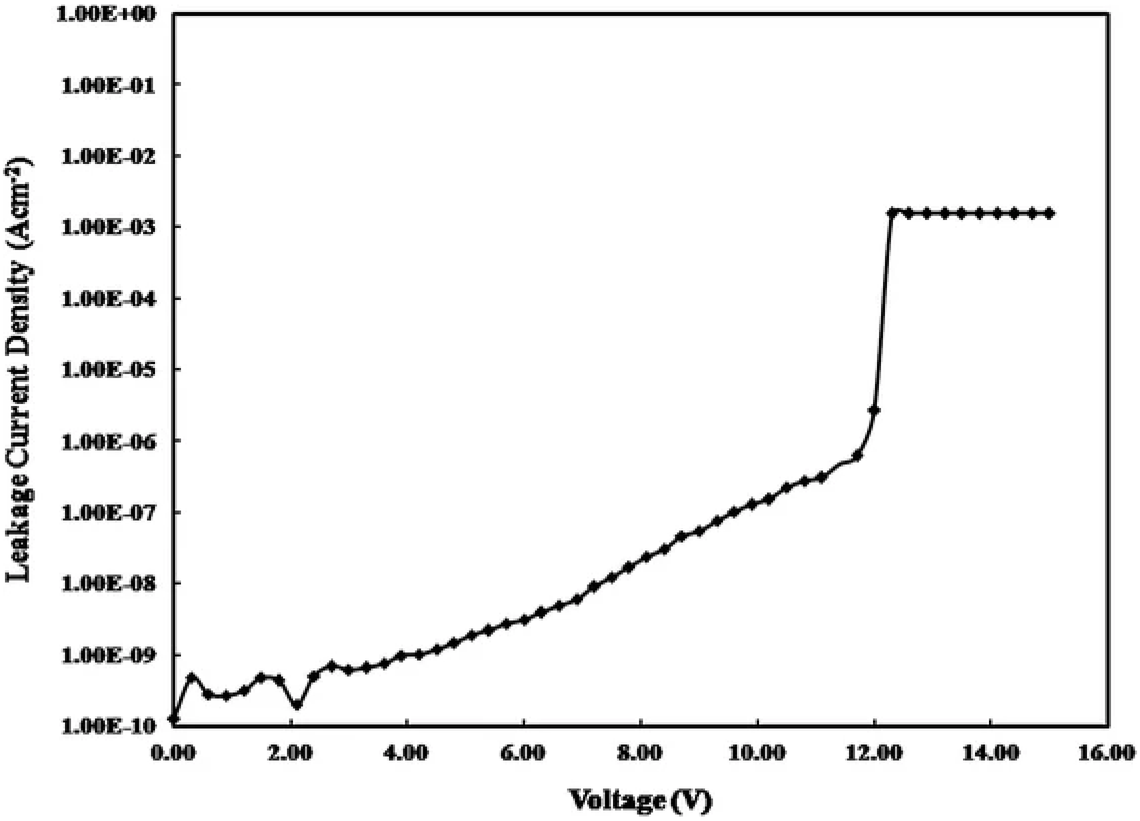

Fig. 6 J–V characteristics of the 35.38-nm thin HfO2 films.

Conclusion:

The HfO2 films exhibited a crystalline structure, as verified by XRD, and chemical analysis revealed the presence of both hafnium oxide and silicon oxide in the films. The sample deposited for 7 minutes showed an effective dielectric constant (k) of 7.99, demonstrating good dielectric properties and low leakage current density. The measured Q-eff and Dit indicated minimal trap charges within the oxide and at the oxide–semiconductor interface. These results highlight that HfO2 is a promising candidate for use as a crystalline gate dielectric material in the next generation of CMOS devices.

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