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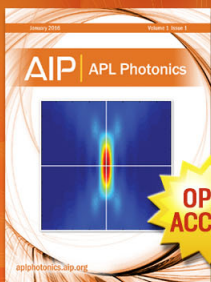
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Hafnium oxide films by atomic layer deposition for high- κ gate dielectric applications: Analysis of the density of nanometer-thin films

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The density of hafnium oxide films grown by atomic layer deposition for high- κ gate dielectric applications was investigated for films with thickness in the nanometer range. The density, measured by combining the film thickness from transmission electron microscopy with the amount of hafnium deposited from Rutherford backscattering, decreased with decreasing film thickness. The dielectric constant of hafnium oxide remained constant with decreasing film thickness, however. The main reason for the decrease in the measured density seemed not to be a decrease in the inherent material density. Instead, the relative importance of interface roughness in the density measurement increased with decreasing film thickness. © 2005 American Institute of Physics. [DOI: 10.1063/1.1866219]

HfO₂ layers manufactured by atomic layer deposition (ALD) are amongst the most promising high- κ candidates to meet the requirements for replacing the SiO₂ gate oxide in complementary metal-oxide-semiconductor devices, when the equivalent oxide thickness (EOT) approaches 1.0 nm.¹ As the target physical thickness of high- κ films is determined by the ratio of their dielectric constant κ (for HfO₂ ~ 20) and that of SiO₂ (3.9) times the EOT,¹ for reaching EOTs 1.0 nm and below, the target thickness of HfO₂ films is about 5.0 nm and below.

Density is one property critically related to the electrical performance of the layers: low κ and high leakage currents are expected for poorly structured films with a low density. Decreasing density with decreasing thickness has been reported for ALD-grown TiN films,² but the origin of the observations is not known. Little is currently known of the density of nanometer-thin ALD-grown HfO₂ films,³ and in this work, we analyze the density of such films.

Density was measured by combining the film thickness from transmission electron microscopy (TEM) with the amount of hafnium deposited from Rutherford backscattering (RBS). HfO₂ films were grown by ALD on *p*-type Si (100) wafers from HfCl₄ and H₂O reactants at 300 °C. Before ALD, the wafers were cleaned to remove the native oxide, after which a chemical silicon oxide was grown with a thickness of about 1.0 nm.⁴ HfO₂ films grown on this surface were amorphous in x-ray diffraction, when the number of ALD reaction cycles was below 200. Cross section TEM specimens were prepared by conventional ion milling and observed in Philips CM30 TEM operating at 300 kV. Because the contrast in the layers changed somewhat gradually, minimum and maximum thickness h^{TEM} (nm) were deter-

mined from TEM. The areal density of Hf atoms c_{Hf} (nm⁻²) was detected by RBS using 1–2 MeV He scattering. The measured density ρ_m (g cm⁻³) was obtained by combining the TEM and RBS measurements:

$$\rho_m = (c_{\text{Hf}}M)/(N_A h^{\text{TEM}}), \quad (1)$$

where M is the molar mass of HfO₂ (g mol⁻¹) and N_A is Avogadro's number (mol⁻¹).

The HfO₂ thickness measured by TEM h^{TEM} increased approximately linearly with the Hf areal density c_{Hf} , as seen from Fig. 1(a). For reference, the areal densities have been converted to a "RBS thicknesses" h^{RBS} through

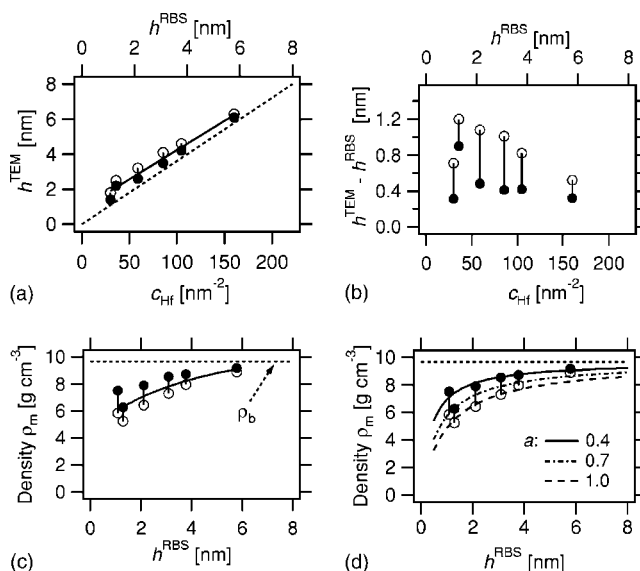


FIG. 1. Analysis of density of ALD-grown HfO₂ films: (a) the h^{TEM} and (b) $h^{\text{TEM}} - h^{\text{RBS}}$ as function of c_{Hf} and h^{RBS} ; (c) the apparent density ρ_m calculated by combining h^{TEM} and c_{Hf} [Eq. (1)]; and (d) the ρ_m simulated with Eq. (5), assuming $b=0$ and a as indicated. The data points correspond to 20, 30, 40, 60, 80, and 120 ALD reaction cycles; bulk density ρ_b of 9.68 g cm⁻³ is shown.

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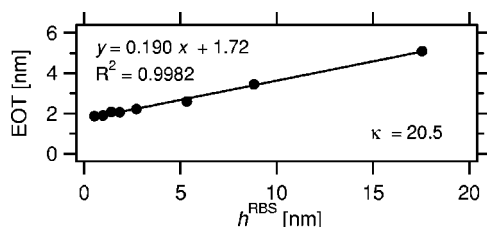


FIG. 2. Results of C - V measurements for HfO_2 capacitors (10–400 ALD reaction cycles on an interface of 1 nm SiO_2 +3 nm Al_2O_3). A linear dependency of EOT on h^{RBS} indicates that the κ of nanometer-thin HfO_2 films is independent of film thickness.

$$h^{\text{RBS}} = (C_{\text{Hf}}M)/(\rho_b N_A), \quad (2)$$

assuming that the HfO_2 is stoichiometric and has the bulk density $\rho_b = 9.68 \text{ g cm}^{-3}$.^{3,5,6} The h^{TEM} is about 0.3–1.2 nm higher than the h^{RBS} [Fig. 1(b)].

The measured HfO_2 densities ρ_m calculated through Eq. (1) are shown in Fig. 1(c). With increasing h^{RBS} , ρ_m approaches the expected bulk density ρ_b . With decreasing h^{RBS} , in turn, ρ_m decreases to values significantly below ρ_b , down to about 60% for $h^{\text{RBS}} \approx 1$ nm. As seen by combining Eqs. (1) and (2), the measured density ρ_m is simply the ratio of the thicknesses determined by TEM and RBS, multiplied by the bulk HfO_2 density:

$$\rho_m = (h^{\text{RBS}}/h^{\text{TEM}})\rho_b. \quad (3)$$

It is therefore the difference between h^{TEM} and h^{RBS} , about 0.3–1.2 nm, which accounts for the low ρ_m values.

To investigate whether the low ρ_m affects the dielectric constant κ of HfO_2 , capacitance–voltage (C - V) measurements were made for capacitors prepared on an interface of about 1 nm SiO_2 +3 nm Al_2O_3 , with a TiN electrode.⁷ The EOT, calculated from capacitance extracted by Hauser fitting, scaled down linearly with HfO_2 thickness (Fig. 2). If the low ρ_m would be reflected in the C - V measurements, one would expect the κ to decrease with decreasing film thickness, giving a higher slope of EOT versus h^{RBS} for smaller thicknesses. The constant slope indicates, however, that the low ρ_m is not reflected in the κ .

To understand why the low ρ_m is not reflected in the value of κ , we analyze the reasons behind the low observed ρ_m . If the films would have atomically sharp interfaces and consist of 100% of the desired material, the h^{TEM} and h^{RBS} would be equal, and we would have $\rho_m = \rho_b$ [Eq. (3)]. However, several factors can influence the observed h^{TEM} (Fig. 3).

(i) Roughness of the substrate–film bottom interface increases the h^{TEM} . This roughness originates from the rough-

ness of the original substrate; for example, the current substrate has an rms roughness of about 0.2 nm (denoted r_{bottom}), as measured by atomic force microscopy (AFM).⁸

(ii) Roughness of the top surface of the film also increases the h^{TEM} . The top surface roughness may consist of three components. (a) The roughness of the substrate: the ALD-grown film follows the substrate conformally, copying also its roughness. In accord with this fact, the AFM rms roughness for the ALD-grown HfO_2 was measured as about 0.2 nm. (b) Atomic-scale roughness originating from the ALD process: when less than a monolayer of material is deposited per cycle, atomic-scale roughness is created through the presence of partly filled material layers.^{9,10} At least one partly filled material layer will in any case be present. However, it may be too ideal to assume that one material layer would get completely filled before deposition begins in another layer. Therefore, we assume about two monolayers as a more reasonable estimate for the atomic-scale roughness, corresponding to about 0.6 nm. (Analysis of the density, to follow, will show that this is a reasonable estimate.) This atomic-scale roughness will most likely not be seen by AFM, because the AFM tip cannot penetrate openings narrower than the tip diameter. (c) Crystallization may occur during the ALD growth, increasing the roughness with film thickness.^{11,12} Such effect was not noticed in AFM measurements for the current samples (up to 120 ALD reaction cycles), however. We estimate the summed top surface roughness as about 0.2+0.6 nm=0.8 nm (denoted r_{top}).

(iii) Island-like morphology of the ALD-grown films can increase the h^{TEM} .^{13–15} Although this contribution may be important on other substrates, on chemically grown silicon oxide, it seems to be of no importance (denoted $r_{\text{isl}} \approx 0$ nm).¹⁶

(iv) Impurities in the bulk HfO_2 film may decrease the film density. ALD-grown HfO_2 films contain at least residual chlorine and hydrogen.^{5,14,17–21} The bulk impurities would increase the h^{TEM} by a factor proportional to the total amount hafnium deposited [denoted $i_{\text{bulk}} \times h^{\text{RBS}}(\text{nm})$].

(v) Impurities present at the substrate–film bottom interface may increase the h^{TEM} . Especially chlorine is known to accumulate at the HfO_2 –substrate interface.^{18–21} Our total reflection x-ray fluorescence and time-of-flight secondary ion mass spectrometry investigations suggest an interfacial chlorine areal density of about 2.5 nm^{-2} .²² Calculating the volume of the chlorine atoms from the van der Waals radius of 0.175 nm,²³ and converting this volume to a thickness indicates that the chlorine impurities could increase the h^{TEM} by about 0.05 nm (denoted i_{bottom}).

(vi) Atoms not to be included in the HfO_2 film, such as hydrogen atoms in OH groups, are present at the top film

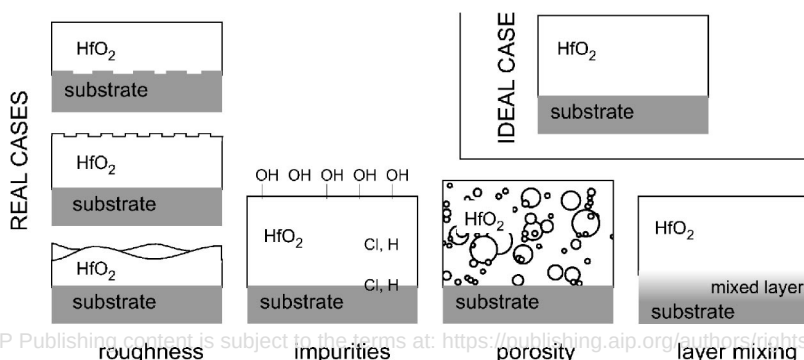


FIG. 3. Factors that may increase the h^{TEM} compared to an ideal HfO_2 film (atomically sharp interfaces, no impurities): (a) roughness of the interfaces, (b) impurities in the film and at the interfaces, (c) porosity, and (d) mixing at the substrate–film interface.

surface. In principle, they may increase the h^{TEM} , if they give a similar contrast as the HfO_2 , but in our case it is not expected (we denote $i_{\text{top}} \approx 0$ nm).

(vii) Porosity could account for film densities lower than the bulk density. It would increase the h^{TEM} by a factor that is proportional to the total amount of hafnium deposited [denoted $p_{\text{bulk}} h^{\text{RBS}}(\text{nm})$].

(viii) Mixing could take place between the substrate and the HfO_2 at the bottom interface, which would add a contribution to the h^{TEM} . For example, the formation of a hafnium silicate layer between the ALD-grown HfO_2 and the substrate has been proposed.^{20,24} Even if no silicate phase forms,²⁵ there is a discontinuity between the SiO_x and HfO_2 , which is likely to alter the local HfO_2 structure. We cannot reliably estimate how much this effect increases the observed film thickness, and we denote $m_{\text{bottom}} = x(\text{nm})$. Our x-ray photoelectron spectroscopy (XPS) and TEM measurements together indicate that $x \leq 0.6$ nm.²⁶

Summarizing, there are two types of contributions that may increase the h^{TEM} compared to h^{RBS} : terms approximately independent of the film thickness, denoted together as a [$a = r_{\text{bottom}} + r_{\text{top}} + r_{\text{islands}} + i_{\text{bottom}} + i_{\text{top}} + m_{\text{bottom}} \approx (1.05 + x)\text{nm}$], and terms approximately proportional to the film thickness, denoted together as b ($b = i_{\text{bulk}} + p_{\text{bulk}}$). Therefore, we expect the following correlation to describe h^{TEM} :

$$h^{\text{TEM}} = a + (1 + b)h^{\text{RBS}}. \quad (4)$$

Combining Eqs. (3) and (4), the measured density is

$$\rho_m = [h^{\text{RBS}} / (a + (1 + b)h^{\text{RBS}})] \rho_b. \quad (5)$$

We analyze separately the importance of a and b in determining the measured density. For thicker films ($h^{\text{RBS}} \gg a$), b dominates in determining ρ_m , whereas for thinner films ($h^{\text{RBS}} \sim a$), a dominates. For thicker films, densities close to the expected bulk density of 9.68 g cm^{-3} have been measured.^{3,5,6} Furthermore, according to our experiments, the difference between h^{TEM} and h^{RBS} does not increase with h^{RBS} (Fig. 1(b)). Both results indicate that $b \approx 0$. Consequently, the films seem to be nonporous ($p_{\text{bulk}} \approx 0$) and to contain so little bulk impurities that the impurities do not affect the measured density ($i_{\text{bulk}} \approx 0$). We must have $a > 0$ to explain the low observed densities.

The estimate obtained for a by summing the effect of all the terms in items (i)–(viii), $a \approx (1.05 + x) \text{ nm}$, is close to the experimentally determined difference between h^{TEM} and h^{RBS} , about 0.3–1.2 nm. As the origin of the low ρ_m values, therefore, we identify most importantly the roughness of the interfaces. The density appears to decrease with decreasing h^{RBS} , because it follows a function of type $\rho_m / \rho_b = f(x) = x / (a + x)$, where $x = h^{\text{RBS}}$. The effect of a to the measured density is further illustrated in Fig. 1(d): with a between 0.4 and 1.0 nm, the simulated and measured ρ_m values agree.

In conclusion, we have measured significantly lower apparent density for nanometer-thin ALD HfO_2 films than the expected bulk density. However, the low apparent density was not reflected in physical properties of the HfO_2 films, such as the dielectric constant. The decrease in measured density with decreasing film thickness appeared to be an artifact: atomic-scale interface roughness hampered the density determination for nanometer-thin films. Similar difficulties in density measurements are expected for other nanometer-thin material films as well.

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