Structural and electrical properties of Dy and Ta co-substituted (Hf, Zr)O₂ ceramics as a novel high-k dielectric for logic and memory devices

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Abstract: Ceramic Hf₀.₂Zr₀.₆Dy₀.₁Ta₀.₁O₂ (HZDTO) has been synthesized by mixing stoichiometric HfO₂, ZrO₂, Dy₂O₃, and Ta₂O₅ through solid-state reaction route. Single-phase material was formed at 1600°C by calcination for 8 hours as revealed by X-Ray Diffraction analysis. Ceramics were then prepared from uni-axially pressed pellets by sintering at 1600°C. The surface morphology and composition of these pellets were studied with field emission scanning electron microscopy and Energy-Dispersive X-ray (EDX). From the electrical measurements, it is found that dielectric constant and the loss tangent HZDTO are ~29 and ~ 0.04, respectively at 100 kHz. The current-voltage (I-V) and capacitance-voltage (C-V) characteristics of the metal/ceramic/metal are discussed. Frequency and temperature dependence of the ac-conductivity were studied with an impedance analyzer. Based on the results, conclusions were drawn on the applicability of HDZTO material for logic and memory devices.

Keywords: Gate oxides, HZDTO, Structural properties, Morphological and Electrical Characterization

1. INTRODUCTION

The standard SiO₂-SiON-Si₃N₄ gate oxide with a dielectric constant (k) in the range ~ 3.9-7 posed serious leakage current issues for the microprocessors when the equivalent oxide thickness of the gate-dielectric (~1.2 nm) corresponding to 3-4 monolayer is reached for 45 nm technology node in 2007 [1-2]. The oxides of Zr, Hf, and their silicates are used then in microelectronics devices and HfSiON (k>14) is the currently used gate-oxide in logic devices. This composition is having the option of increasing the dielectric constant up to 25, if the Hf content is increased at the cost of Si. However, increasing the Hf content increases the trap related leakage current and the formation of a dead layer that additionally can pose a serious problem in realizing sub-nanometer equivalent oxide thickness. This force the introduction of another oxide having high dielectric constant (high-k) >25, good thermodynamic stability (up to 1000 K), large conduction/valence offset with Si (above 1 eV), and large bandgap (above 5 eV) in the semiconductor industry for the sub-nanometer technology node
as per the Moore’s law. In this context, a wide range of binary and complex oxides are emerged as a potential contender like ZrO$_2$, HfO$_2$, SrTiO$_3$, BaSrTiO$_3$, DyScO$_3$, LaAlO$_3$, HfO$_2$, HfAlO, LaGdO$_3$, PrScO$_3$, GdScO$_3$, LaLuO$_3$ [3-7]. From the knowledge acquired from the high-k gate oxide research of the last three decades, Intel has come up with a noteworthy revolution using HfO$_2$ and ZrO$_2$ high-k dielectric to replace the conventional HISION dielectric in ≤ 22nm technology node [3]. However, binary oxides like HfO$_2$ and ZrO$_2$ accounted for high defect concentrations with respect to ‘O’ vacancies, resulting in a large threshold voltage shift [5]. Inter-lanthanides and scandates can also have a high physical thickness for achieving the required equivalent oxide thickness (EOT) for the sub-nanometer technology node. Scaling down the electronics devices for high density and speed, these materials are actively considered at present.

For the Process Integration, Devices, and Structures the International Technology Roadmap semiconductor (ITRS) forecast the EOT for high-performance technology devices in logic processor and memory devices [8]. The reduction in gate-induced leakage current and nano-capacitor in the future are the key aspects that need another gate material for the logic devices and memory devices, respectively. The high temperature (400°C or above) annealing disturb the interface among high-k oxide and metal gates [9]. The discovery of ferroelectricity in doped HfO$_2$ and (Hf, Zr)O$_2$ gained interest in CMOS as it can be of immense potential in realizing high-density non-volatile memory[6]. Also, ternary oxides of (Hf, Zr)O$_2$ show high dielectric constant, but it shows ferroelectricity detriment for the gate-oxide application. In the same material (Hf, Zr)O$_2$, by doping with another CMOS friendly material to realize a linear high-k material is worth considering. In this context, a controlled amount of Dy and Ta addition is considered to increase the dielectric constant to 30 without compromising the bandgap and band offset with the semiconductor. Dy and Ta substitution is considered in the (Hf, Zr)O$_2$ lattice as Dy$^{3+}$ and Ta$^{5+}$ in equal molar amount ensure charge neutrality of the resulting composition. The relative dielectrics constant $\varepsilon_r$ of compounds can be determined by using Clausius-Mosotti equation (1):

$$\varepsilon_r = \frac{(3V_m + 8\pi\alpha)}{(3V_m - 4\pi\alpha)}$$  \hspace{1cm} (1)

The relative permittivity value of (Hf, Zr) (Dy, Ta) O$_2$ needs to be evaluated using equation (1) stating Zirconium (Zr), Dysprosium (Dy), and Tantalum (Ta). Here, $V_m$ is the molar volume of the material with total dielectric polarizability (\(\alpha\)) of 2.01Å (O$^{2-}$), 3.81Å (Hf$^{4+}$), 2.04Å (Zr$^{4+}$), 4.07Å (Dy$^{3+}$), 4.73Å (Ta$^{5+}$) respectively, from Shannon’s table [8]. We report the synthesis and characterization of Hf$_{0.2}$Zr$_{0.8}$ Dy$_{0.1}$Ta$_{0.1}$O$_2$ ceramics. Its dielectric properties with respect to temperature and frequency along with the leakage current and conductivity are scrutinized for the possible application as a gate-oxide as well as a volatile memory capacitor in DRAM. The rest of the paper is arranged as follows; Section 0 describes experiments performed followed by results and discussion in Section 0. Finally, conclusion of the present study is given in Section 0.

2. EXPERIMENTAL DETAILS

The synthesis of single-phase HZDTo powder was done first using a solid-state reaction. For this powder preparation, HfO$_2$ (99%), ZrO$_2$ (99.7%), Dy$_2$O$_3$ (99.9%) and Ta$_2$O$_5$ (99 %) with the stoichiometric mixture 9HfO$_2$:6.0747 gm, ZrO$_2$:10.5935 gm, Dy$_2$O$_3$:5.3393 gm, Ta$_2$O$_5$:6.3765 gm) were mechanically ball-milled in ethanol for 10 hours and later heated at 100°C on a hot plate to evaporate the organic solvent. The composition of the powder is (Hf$_{1/2}$, Zr$_{3/2}$, Dy$_{1/2}$, Ta$_{1/2}$)$_2$O$_2$. These resulting powders were then undergone high energy ball milling in acetone media for 5 hours. The milled powder was then dried, and calcined at various temperatures 1100 to 1600°C from 4 to 12 hours using a Carbolite HTF1700 furnace, with a heating and cooling rate of 15°C/min. This calcination step as a function of temperature and time was the optimization process to realize single phase formation of the (Hf$_{0.2}$, Zr$_{0.8}$) (Dy$_{0.1}$, Ta$_{0.1}$)O$_2$ powder.
The synthesized single-phase HZDTO powders with 7 wt% polyvinyl alcohol were uni-axially pressed at 3 Tons that resulted in green compacts having a density of ~ 50% of theoretical density. The green compact was later sintered at 1600°C for 4 hrs for densification. Ceramic pellets having a diameter (φ = 7 mm) and thickness (t=1mm) were used for the bulk characterization. The microstructural and compositional analysis of the sintered pellet was carried out using a Scanning Electron Microscope (SEM) and EDX, respectively. For dielectric characterization, (Hf\textsubscript{0.2}, Zr\textsubscript{0.6})(Dy\textsubscript{0.1}, Ta\textsubscript{0.1})O\textsubscript{2} pellets were coated Pt thin films to form the top and bottom electrodes by DC sputtering. The resulting Metal-Insulator-Metal (MIM) structures were annealed at 400°C in air for proper adhesion of Pt and recovery of the possible sputter damage induced during the electrode deposition. The dielectric and DC leakage current measurements were done under vacuum (10\(^{-6}\) Torr) with HP 4294A Impedance Analyzer and Keithley electrometer (model #6517A), respectively. The temperature control was achieved using a programmable temperature controller [MMR Technologies, Incorporation]. The samples were kept in dark during electrical measurements.

3. RESULTS AND DISCUSSION

The obtained results are segregated into structural, morphological, electrical properties and are discussed below.

3.1. Structure and Surface Morphology

The structural evolution of the single-phase formation of HZDTO powder is studied as a function of calcination temperature with X-ray Diffraction (XRD). The XRD pattern of (Hf\textsubscript{1/4}, Zr\textsubscript{3/4})\textsubscript{0.8}(Dy\textsubscript{1/2}, Ta\textsubscript{1/2})\textsubscript{0.2}O\textsubscript{2} calcined at various temperature are shown in figure 1(a). As ball milled sample shows a mixed-phase and contains the monoclinic phases of both ZrO\textsubscript{2} and HfO\textsubscript{2}. Also, reflections corresponding to Dy\textsubscript{2}O\textsubscript{3} and Ta\textsubscript{2}O\textsubscript{5} were also observed in the XRD pattern of the ball billed powder. However, as the calcination increased solid-state reaction between occurs Hf, Zr, Dy, and Ta diffuse into the lattice and structure starts to evolve into a single phase. For about 1600°C single phase HZDTO is formed and the observed peak splitting around 30 may be due to the tetragonal splitting of (110) and (011). Further studies are in progress to find the exact structure of this particular composition. The energy dispersive x-ray analysis of the pellet revealed is depicted in figure 1(b). Energy dispersive X-ray (EDX) analysis of the sintered ceramic (Hf\textsubscript{0.2}, Zr\textsubscript{0.6})(Dy\textsubscript{0.1}, Ta\textsubscript{0.1}) showed Zr/Hf molar ratio ~ 3, Dy/Ta~1 and Zr/(Hf+Dy+Ta) ~ 1.5. So, the pellet is nearly stoichiometric within the experimental error of EDX.

![Figure 1](image1.png)

Figure 1.(a) X-ray diffraction patterns of as-ball milled, calcined at 1500°C,1600°C HZDTO powder and (b) EDX spectrum of the HZDTO ceramic.

The surface morphology of the pellets is studied with scanning electron microscopy. SEM images of two different magnification such as 10μm (as shown in figure 2(a)) and 5μm (as shown in figure 2(b))
for the sample sintered at 1600°C for 8 hours. The uniform grain formation with interlinked grain suggesting high density and low porosity as can be seen in figure 2(a) as well as in and figure 2(b).

![Figure 2. FE-SEM images with two different magnification; (a) 10μm and (b) 5μm of HZDTO ceramic sintered at 1600°C.](image)

3.2. Electrical Properties

The frequency and temperature dependence of dielectric constant, $\varepsilon_r$, and dielectric loss, $\tan \delta$ for HZDTO ceramics are illustrated in figure 3. The applied ac signal level was 500 mV. As can be seen from figure 3, the dispersion was less between 100 Hz to 1 MHz as the dielectric constant was independent of frequency for the temperatures between 175 to 375°C. However, at the higher temperature, 400 to 475°C dielectric constant is slightly dependent on the temperature. A similar trend was observed for the dielectric loss as well. The high value of dielectric constant around 29 is interesting for the targeted high-$k$ gate oxide application. However, leakage current and capacitance-voltage characteristics are of primary importance for such application and will be discussed now.

![Figure 3. Temperature variation of $\varepsilon_r$ and $\tan \delta$ of HZDTO ceramics.](image)

The leakage behavior of HZDTO is shown in figure 4 (a). Current was measured after applying a dc electric field that starts from 0 V/cm to 8 V/cm then back to 0 V. The same is continued to the -8 V/cm and then to 0 V/cm. Currents were measured after giving a proper delay at each voltage step. The leakage current ($J_{\sigma}$) was as low as $3 \times 10^{-19}$ A/cm$^2$ at an electric field $=8$ V/cm. The figure 4(b) shows the C-V curve for 100 Hz, 1 kHz, 10 kHz, 100 kHz, and 1 MHz With the application of voltage, the capacitance changes negligibly. The linear outcomes (i.e. no hysteresis loss) obtained from -40 V to +40 V are interesting for the gate-oxide applications.
For an electrode area (A), applied voltage ($V_0$), and the thickness of the dielectric (d), dc electrical conductivity ($\sigma_{dc}$) can be given by the equation (2):

$$\sigma_{dc} = \frac{dI_0}{AV_0}$$

Also, electrical conduction is a thermally activated process and hence, $\sigma_{dc}$ follows Arrhenius equation:

$$\sigma_{dc}(T) = C \exp\left(\frac{E_A}{k_B T}\right)$$

Here, $k_B$ is the Boltzmann constant, $T$ is the temperature in °K, $C$ is a constant, $E_A$ is the activation energy for dc-conduction, and is evaluated from slope of the plot log $\sigma_{dc}$ vs $T^{-1}$

Some material having a low concentration of bonded ions, bear low dc current value and hence are not accurately measured. The impedance spectroscopy is one of the ac techniques for the determination of the electrical properties of materials. So, to reduce the ambiguity, AC electrical conductivity of this high-k material is also evaluated with the help of impedance spectroscopy. The electrode polarization effect gets reduced for above some frequencies. The ac electrical conductivity, $\sigma_{ac}$ can be calculated from the measured dielectric data and angular frequency ($\omega=2\pi f$) with the help of equation (3):

$$\sigma_{ac} = \omega \varepsilon_r \varepsilon_0 \tan \delta$$

where, $\varepsilon_r$, tan $\delta$ are the dielectric constant, dielectric loss of the material measured/calculated with the impedance analyzer respectively and $\varepsilon_0$ is the dielectric permittivity of vacuum. Dependence of $\sigma_{ac}$ on the frequency at various temperatures is shown in figure 5(a). The variation of $\sigma_{ac}$ with an increase in frequency denotes that the conductivity is not entirely because of free carriers and bound carriers also contribute like hopping conduction and Maxwell-Wagner conduction [10]. In the case of Maxwell-Wagner dispersion arises with the presence of interfacial polarization of inhomogeneous dielectric structure and total electrical conductivity can be written as equation (4):

$$\sigma_{ac} = \sigma_{dc} + A\omega n1 + B\omega n2$$

where, A, B, n1, and n2 are material-dependent constant. Also 0 < n1 < 1, 1 < n2 < 2. The conductivity increases with an increase in temperature, shown in figure 5(b). The low activation energy ($E_A$ gave in equation (2b)) suggests the non-equilibrium state while high activation energy suggests the mobility of oxygen ions are responsible for the conduction. The vacancy of oxygen is
more at elevated temperature and migration of corresponding ions occur and hence high conductivity at elevated temperatures.

![Graph](image)

**Figure 5.** The ac conductivity variation (a) with frequency, and (b) with inverse of absolute temperature ($10^3/T$).

4. CONCLUSION

(Hf$_{0.8}$, Zr$_{0.8}$)(Dy$_{0.2}$, Ta$_{0.2}$)O$_2$ (HZDTO) ceramics were successfully prepared through a solid-state reaction route. The capacitance-voltage characteristics of the MIM structure have negligible hysteresis and were voltage-independent. The dielectric constant, $\varepsilon_r$ is 28.75 and loss tangent, $\tan \delta$ is 0.04 for HZDTO ceramics. The leakage current of the capacitor was low. As one of the encouraging materials with high dielectric constant, large barrier height, large bandgap, and low leakage current, HZDTO has the potential for future memory and logic devices. In short, characteristics of the bulk HZDTO are suitable for gate-oxide applications in future logic devices and for that ultra-thin film deposition and testing are needed.

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