Hf-Based High- κ Dielectrics: A Review

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In the last decades, the number of transistors per chip with integrated circuits has increased leading to reduction in the thickness of silicon dioxide used as gate dielectrics. However, at small dielectric thicknesses leakage current formation has begun due to the quantum tunneling effect. Thus, it became essential to replace SiO_2 with alternative dielectrics with high dielectric constant to maintain the same capacitance at higher gate dielectric thicknesses. This review analyzes alternative high- κ dielectric materials substituting for SiO_2 . For this reason, the properties of materials with high dielectric constant are compared to SiO_2 with a special emphasis on HfO_2 , since it is the most promising high- κ dielectric to replace SiO_2 . The fundamental points concerning HfO_2 gate dielectrics are their high dielectric constant and their thermodynamic stability when in contact with Si. In this article, properties of HfO_2 fabricated with different coating methods and doped with different elements such as N, Si, Al, Ti and Ta have been compared and discussed. In the conclusion part, we have summarized the results of characterization obtained by X-ray diffraction, scanning electron microscopy, leakage current density-voltage (J - V), capacitance-voltage (C - V) and UV-vis spectroscopy of HfO_2 thin films.

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1. Introduction

Silicon oxide has been utilized as gate dielectric material for over 40 years [1]. However, progressive minimization of transistor dimensions requires the gate oxide layers with very low thickness leading to unwanted leakage currents due to the tunneling effect. To solve this problem, alternative gate dielectric materials have been investigated with higher dielectric constant (high- κ) than that of SiO_2 . These high- κ candidates are Ta_2O_5 , TiO_2 , ZrO_2 , Al_2O_3 , HfO_2 , HfO_xN_y , HfSi_xO_y , HfAl_xO_y , or nitrided SiO_2 and Zr-based oxides. These candidates should have high dielectric constant and be thermally stable when in contact with Si. Oxides of metals from group 2A like CaO and the high- κ oxides such as TiO_2 , Ta_2O_5 and Nb_2O_5 have not been preferred in the electronic circuits because of their reactivity with Si. Therefore, dielectrics alternative to SiO_2 are restricted to the high- κ oxides such as HfO_2 , ZrO_2 , Al_2O_3 , Y_2O_3 , and La_2O_3 . Among these candidates, HfO_2 gate dielectric layers are the most suitable materials because of their thermal, electrical, and mechanical properties [2–8].

High- κ gate oxides emerged into the market with Intel's new generation 45 nm microprocessors in 2007. Next, Intel produced high- k /metal gates with 32 nm width in 2009. In both transistors, silicon oxide-based insulator has been replaced by hafnium-based oxides. Furthermore, polycrystalline silicon gates were substituted with metal-gates [9, 10]. In 2011, 22 nm chips, using high- k gate dielectrics, were demonstrated based on 3D tri-gate transistor architecture by Intel. Then, Intel started mass production of 14 nm microprocessors

formed by 3D transistors in 2014 using the same gate oxide layer [11–13]. Afterwards, Samsung announced 10 nm FinFET (fin field effect transistor) technology on February 23, 2017. FinFET is a 3D double-gate transistor set up, where the gate is positioned on multiple sides of the channel or wrapped around the channel, forming a double gate structure. By means of this structure, transistors with smaller gate lengths can be produced with increased efficiency and performance. For instance, 10 nm FinFETs bring up 27 percent higher performance and 40 percent less power consumption than 14 nm FinFETs [14, 15]. In the following years, Samsung has released details on the 7 nm FinFET technology with EUV (extreme ultraviolet) lithography and started mass production of FinFET with higher performance and lower power consumption on October 18, 2018 [16, 17]. Samsung had set a course for FinFET technology since 2016 and FinFET process technology will proceed with 5 nm 2019, 4 nm 2020 and 3 nm 2021 [18]. On January 7, 2019, Intel introduced 10 nm Ice Lake processors that have high- k metal gate transistors with 3D structures [19].

2. Gate dielectrics

According to the Moore's law, it is predicted that the dimensions of the transistors will shrink every 2 years. With advancing technology, as the dimensions of the dielectric material diminish, the number of transistors per chip increases. In addition to size shrinking, performance and functionality of the new generation transistors also improve (Fig. 1). Moreover, the cost of the circuits reduces biennially [20, 21]. As the gate length of transistors decreases, the thickness of the gate oxide layer should also decrease to maintain the same performance. However, thickness of the gate oxide layer below 1 nm causes high leakage currents due to the tunneling effect [2, 6]. To use

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thicker oxide layers and maintain the same performance, SiO_2 should be replaced by high dielectric constant oxides in the new generation transistors. A high κ value provides lower equivalent oxide thickness (EOT) and higher the gate capacitance at the desired thickness. The EOT can be calculated as

$$\text{EOT} = d_{\text{Hik}} \frac{K_{\text{SiO}_2}}{K_{\text{Hik}}}, \quad (1)$$

where d_{Hik} is the thickness of the dielectric layer, K_{SiO_2} is the dielectric constant of silicon dioxide and K_{Hik} is the dielectric constant of gate oxide.

In addition, convenient gate oxide layers must have the band offset values of at least 1 eV in order to prevent leakage currents. High- κ oxides with over 5 eV band gaps tend to satisfy this value and hinder flux of electrons or holes into the oxide layers. However, κ values of most dielectric materials are inversely proportional to the band gap value as shown in Table I [21–23].

TABLE I

Comparison of dielectric constant and band gap for various dielectric materials [24–28].

Dielectrics	Dielectric constant (κ)	Band gap [eV]
Si	–	1.1
SiO_2	3.9	9
Si_3N_4	7.5	5
ZrO_2	25	5.8
Y_2O_3	15	5.6
La_2O_3	30	6
Al_2O_3	10	8.8
TiO_2	80	3.5
Ta_2O_5	22	4.4
HfO_2	22–25	5.5–6
LaAlO_3	30	5.6
SrZrO_3	24–27	5.7

Optical band gap of the dielectrics can be analyzed by UV–vis spectroscopic techniques. The band gap of a semiconductor is related to absorbance and photon energy in the following Eq. (2):

$$\alpha h\nu = B(h\nu - E_g)^m \quad (2)$$

where α is the absorption coefficient, $h\nu$ is the photon energy, E_g is the optical band gap, B is a constant and m is a constant related to different electronic transitions for direct allowed $m = 1/2$, indirect allowed $m = 2$, direct forbidden $m = 3/2$ and indirect forbidden $m = 3$ transitions. First, the graph of optical absorption coefficient (α) with photon energy is acquired. Then, extrapolation the straight-line part of the curves to zero absorption coefficient value reveals the optical energy band gap value [29].

Dielectric materials are preferred to have amorphous structure, because leakage current occurs more frequently in crystalline structures than in amorphous structures due to presence of grain boundaries [30].

Fig. 1. Moore's law scaling [31].

The selection criteria of a new high- κ dielectric is as follows: dielectric properties, defect chemistry, chemical suitability with the silicon channel and the gate dielectric leakage current value [21]. When these criteria are considered, alternative dielectrics can be listed as $(\text{Ba}_x\text{Sr}_{1-x})\text{TiO}_3$ (BST), Al_2O_3 , Y_2O_3 , La_2O_3 , HfO_2 , ZrO_2 , TiO_2 , Ta_2O_5 and some nitrides, especially Si_3N_4 [21].

BST has high dielectric constant ($\kappa \approx 100$ –700) and low leakage current density of $5 \times 10^{-8} \text{ A/cm}^2$ at 1 V at 30 nm thickness, but it reacts with the Si substrate to form undesirable interfacial layer [21, 32]. Al_2O_3 has many advantages such as a large band gap ($\approx 9 \text{ eV}$) and good thermal stability with silicon substrates [33]. Si_3N_4 has good mechanical properties and corrosion/thermal-shock resistance. However, both Al_2O_3 ($\kappa \approx 9$) and Si_3N_4 ($\kappa \approx 7$) have low dielectric constants [34, 35]. La_2O_3 has a high dielectric constant ($\kappa \approx 27$) and it is thermodynamically stable with Si, but its band gap value is small (4.3 eV) [36]. TiO_2 and Ta_2O_5 have high dielectric constants ($\kappa = 40$ –80 and $\kappa = 25$, respectively), but both are instable with silicon substrates [37–39].

The dielectric constants of materials are interrelated with the structure (i.e., amorphous and crystalline). ZrO_2 and HfO_2 vary from $\kappa \approx 17$ –47 and $\kappa \approx 12$ –17. In addition, HfO_2 is more stable than ZrO_2 if the interaction with the Si substrate is concerned [40, 41]. Moreover, the leakage current of HfO_2 (10^{-3} A/cm^2) is lower than that of ZrO_2 ($4 \times 10^{-3} \text{ A/cm}^2$) under the electric field 1 MV/cm at temperature of 550 °C [42].

HfO_2 thin films have wide band gap of $\approx 5.8 \text{ eV}$, high dielectric constant ($\kappa \approx 25$) and suitable band offset values relative to Si substrate. In addition, they have excellent thermodynamic and chemical stability with Si [43, 44]. Therefore, Hf-based oxides are the strongest candidate materials for replacing SiO_2 gate dielectrics.

3. Hf-based high- κ dielectrics

HfO₂ presents polymorphisms. It crystallizes in monoclinic m-HfO₂ structure at low temperature, which changes to tetragonal t-HfO₂ upon heating and to cubic c-HfO₂ at higher temperatures (Fig. 2) [45]. Experimental results showed that change in the crystal structure of HfO₂ also changes the band gap. The band gaps of c-HfO₂, t-HfO₂, m-HfO₂ and a-HfO₂ (amorphous) are 5.53, 5.79, 5.65, and 6.04 eV, respectively [30, 45].

Fig. 2. Polymorphic transformation of HfO₂ [46].

Generally, amorphous structures are preferred in dielectric materials, because leakage current occurs in crystalline structure due to grain boundaries. Thus, a-HfO₂ is the most preferred structure in electronic and optoelectronic devices [47].

Following defects form in HfO₂ (Fig. 3), interstitial oxygen ($O_i'' = O_i^{2-}$), oxygen vacancy ($V_O'' = V_O^{2+}$) and hafnium vacancy ($V_{Hf}'''' = V_{Hf}^{4-}$) [48].

- Oxygen vacancy defect chemistry in Si-HfO₂ heterostructure can be suggested according to Eq. (3):

- Oxygen interstitial defect chemistry in Si-HfO₂ heterostructure can be suggested according to Eq. (4):

- Hafnium vacancy defect chemistry in Si-HfO₂ heterostructure can be suggested according to Eq. (5):

These defects can adversely affect the performance of devices. Also, they can create an electric field which can change band offsets and disrupt its dielectric properties [49].

It is quite essential to determine thermodynamic stability of HfSi₂ at the HfO₂/Si interface by using isothermal sections and the isopleth calculations. This thermodynamic stability is related to the formation energy of HfSiO₄. The enthalpy of formation for HfSiO₄ is calculated according to Eq. (6) by using the data from Table II. The result of calculation foresees that HfSi₂ is stable below 543.53 K [50]:

$$\Delta H_f^{HfSiO_4} = H(HfSiO_4) - \frac{1}{2}H(HfO_2) - \frac{1}{2}H(SiO_2) \quad (6)$$

Fig. 3. Initial structures of (a) HfO₂ with one oxygen vacancy and (b) HfO₂ with one interstitial for quantum chemical molecular dynamics simulation [49].

TABLE II

First-principles calculation results of pure elements, hypothetical compounds (α , β -Hf), and stable compounds (HfO₂, SiO₂, and HfSiO₄) [50].

Phases	Space group	Lattice parameters [Å]			Total energy [eV/atom]	ΔH^f [kJ/(mol atom)]
		a	b	c		
HCP_A3 (Hf)	$P63/mmc$	3.198	3.198	5.053	-9.8320	0
Diamond_A4 (Si)	$Fd\bar{3}m$	5.468	5.468	5.468	-5.4315	0
Gas (O ₂)	—	—	—	—	-4.7936	0
α -Hf (HfO _{0.5})	$P\bar{3}m1$	3.225	3.225	5.150	-4.7936	-175.511
B-Hf (HfO ₃)	$Im\bar{3}m$	4.364	4.364	4.364	-7.7253	-161.308
Monoclinic (HfO ₂)	$P2_1/c$	5.135	5.194	5.134	-10.2101	-360.563
Quartz (SiO ₂)	$P3_221$	5.007	5.007	5.496	-7.9581	-284.809
HfSiO ₄	$I4_1/amd$	6.616	6.616	6.004	-9.1024	-324.453

3.1. Fabrication methods

HfO₂ thin films have been synthesized by chemical vapor deposition (CVD) [51], atomic layer deposition (ALD) [52], pulsed laser deposition (PLD) [53], plasma oxidation [54], electron beam evaporation [55], molecular beam epitaxy [56], RF magnetron sputtering [57] and sol-gel method [58]. As a precursor, HfOCl₂ (hafnium(IV) oxychloride) [59], Hf (O-i-Pr)₄ (hafnium isopropoxide) [60], Hf(OC₂H₅)₄ (hafnium tetra-ethoxide) [61], HfCl₄ (hafnium tetra-chloride) [58] were used.

Gopalan et al. indicated that HfO₂ films were deposited by CVD on *p*-type Si (100) substrates. Dielectric constant and the EOT of HfO₂ thin films annealed at 600 °C and 700 °C were measured as 22.18 nm, 16.95 nm, and 2.45 nm, 2.73 nm, respectively [62]. Sayan et al. showed that leakage current densities of HfO₂ thin films as-deposited and annealed (crystallized) at 800 °C by using CVD technique were 7.4×10^{-8} A/cm² and 2.6×10^{-5} A/cm² at 1 V, respectively [63].

Hackley and Gougousi deposited HfO₂ films by ALD using the tetrakis ethylmethyl amino hafnium (TEMAHf) as a precursor which were annealed at different temperatures. The root-mean-square (RMS) roughness values of HfO₂ films were between 0.9 and 1.7 nm annealed at different temperatures (400, 700 and 900 °C). Increasing annealing temperature significantly increased surface roughness. According to XRD and FTIR analyses, the films annealed at 400 °C were amorphous, while at 600 °C films crystallized to monoclinic phase [64].

Wang et al. have synthesized HfO₂ films prepared by pulsed laser deposition on Si(100) substrate in air and N₂ atmosphere. Dielectric constant, band gap, and EOT of the films annealed at 500 °C in air were $\kappa = 40.8$, $E_g = 5.30$ eV and 8.68 nm, respectively. These values changed to $\kappa = 25.1$, $E_g = 5.57$ eV and 7.44 nm, when films annealed at 500 °C in N₂ [65]. In another study, Ying et al. have investigated electrical properties of polycrystalline monoclinic HfO₂ dielectrics prepared by pulsed laser deposition. The dielectric constants for as-deposited and 700 °C annealed HfO₂ films were 12.2 and 16.5, respectively. Leakage current densities were measured as 9.8×10^{-8} , 9.2×10^{-7} A/cm² under electric field of +0.75 and -0.75 MV/cm [66].

He et al. have demonstrated HfO₂ films grown on Si(100) by plasma oxidation. Characterization results are summarized in Table III. Both thickness and band gap of the films decreased with increase of annealing temperature [54]. Li et al. found as the highest dielectric constant of $\kappa = 22$ of HfO₂ when the film was annealed at 500 °C by plasma oxidation [67]. Yamamoto et al. have analyzed the relation between leakage current density and EOT of HfO₂ films prepared by remote plasma oxidation. The results showed as the EOT increasing, the leakage current density decreased to 1.7×10^{-6} A/cm² [68].

Ramzan et al. have found that optical band gap energy of e-beam evaporated HfO₂ at different substrate temperatures (25–120 °C) were strongly dependent on the morphology and grain orientation. There was no significant

TABLE III

Electrical results on as-deposited and annealed at 700 and 800 °C samples [54].

Annealing temperature	t-HfO ₂ [nm]	E_g [eV]
as-deposited	43.1	5.77
700 °C	35.0	5.65
800 °C	34.2	5.56

difference in the optical band gap value of the films as the substrate temperature changes. The optical band gap energy of as-deposited and annealed HfO₂ films were between 3.4 and 3.65 eV, and 4.36–4.45 eV, respectively [69]. It was shown that dielectric constant, leakage current density, and EOT of the films deposited by electron beam evaporation were $\kappa = 21.2$, $J = 2 \times 10^{-3}$ A/cm² at 1 V and 0.65 nm, respectively [70].

Leakage current density and EOT of HfO₂ thin films prepared by laser molecular beam epitaxy (LMBE) were characterized by Lu et al. [56]. It was found that leakage current density and EOT of HfO₂ thin films were 1.5×10^{-2} A/cm² (at 1 V) and 1.3 nm, respectively. Yan et al. prepared HfO₂ thin films by atomic oxygen assisted molecular beam epitaxy. In this study, dielectric constant before annealing was 19, which decreased to 17 after annealing [71].

Nath and Roy investigated the effects of annealing temperature on HfO₂ thin films grown by radio frequency sputtering. From the *I*-*V* analyses, the lowest leakage current density of 1.5×10^{-5} A/cm² was measured at -2 V at 600 °C. According to *C*-*V* analyses at the same annealing temperature, the highest dielectric constant $\kappa = 14$ and the lowest EOT=1.3 nm were obtained [72].

Jin et al. investigated the optical and electrical properties in relation to annealing temperatures of HfO₂ thin films deposited on *n*-type Si and quartz substrates by using sol-gel method. The smallest EOT was determined as 3.10 nm when HfO₂ thin films were annealed at 400 °C [43]. HfO₂ thin films were synthesized on *p*-type Si (100) by sol-gel method with high purity by Leu et al. [73]. The results indicated that the thickness and surface roughness values of HfO₂ thin films annealed at 900 °C were 8.2 nm, 10.4 nm and 0.283 nm, 0.257 nm, respectively. Crystallization temperature of the HfO₂ films deposited by sol-gel methods was observed between 500 and 550 °C by Nishide et al. [58].

According to Table IV, the best results of thin films derived from different coating methods are as follows. The highest value of dielectric constant is obtained with pulsed laser deposition method. The lowest values of EOT and leakage current are observed with e-beam evaporation and atomic layer deposition methods. Among them, sol-gel method results in high-quality films in various shapes, sizes and forms. It is also a simple technique, with which the components of a multi-layered structure can be easily controlled. In addition, the process takes place at low temperatures leading to lower cost.

Summary of results of different coating methods [43, 58, 62–76].

TABLE IV

Methods	Advantages	Disadvantages	Electrical properties
CVD	large area growth, good composition control, film uniformity, excellent conformal step coverage	restricted deposit temperature, difficult controlling composition, composition impurity, high cost	$\kappa = 17\text{--}23$ $J = 7.4 \times 10^{-8} \text{ A/cm}^2$ at 1 V EOT = 2.73 nm at 700 °C
ALD	atomic level control of the film thickness, excellent conformal step coverage, ultra-thin films, deposit at low temperature	very slow growth rate	$\kappa = 12\text{--}20$ $J = 2.2 \times 10^{-9} \text{ A/cm}^2$ at 1 V EOT = 0.5 nm at 800 °C
PLD	simplicity, flexibility, maintaining the target stoichiometry, large deposition rate, low growth temperature	relatively difficult to control film composition	$\kappa = 25\text{--}40$ $J = 9.8 \times 10^{-8} \text{ A/cm}^2$ at 0.75 V EOT = 7.44 nm at 500 °C $E_g = 5.57$
plasma oxidation	low growth temperature, high quality, easy controllable growth	difficult controlling composition	$\kappa = 22$ $J = 2.7 \text{ A/cm}^2$ at -1 V EOT = 0.65 nm at 600 °C $E_g = 5.77 \text{ eV}$
e-beam evaporation	control of deposition rates, excellent material utilization, freedom from contamination, good purity	higher surface roughness, relatively difficult to control film	$\kappa = 21$ $J = 2 \times 10^{-3} \text{ A/cm}^2$ at 1 V EOT = 10.9 Å at 400 °C $E_g = 3.65 \text{ eV}$
molecular beam epitaxy	atomic level control of the film thickness, high purity	slow growth rate	$\kappa = 17\text{--}19$ $J = 1.5 \times 10^{-2} \text{ A/cm}^2$ at 1 V EOT = 1.3 nm at 500 °C
RF sputtering	lower contaminants, controllable growth, low temperature process, compositional consistency, low cost	sputtered target plasma induced damage, difficult to deposited complex shape	$\kappa = 14$ $J = 1.5 \times 10^{-5} \text{ A/cm}^2$ at -2 V EOT = 1.3 nm at 600 °C
sol-gel	easy composition control, high purity, large area deposition, low operation cost, better homogeneity for multi-component materials, low temperature process	segregation of gel, cracks and voids during annealing	$\kappa = 15\text{--}22$ $J = 10^{-8} \text{ A/cm}^2$ at 1 V EOT = 3.10 nm at 400 °C $E_g = 5.60 \text{ eV}$

3.2. Commonly used dopants in HfO_2

Doping of HfO_2 gate dielectric provides many advantageous properties. Therefore, HfO_2 has been doped with elements such as N, Si, Al forming mostly interstitial defects or Ti and Ta forming substitutional defects [77, 78].

3.2.1. N-doping

It has been observed that thermal and electrical properties of HfO_2 are improved by N doping. Nitrogen incorporation increases the crystallization temperature enabling the application of higher annealing temperatures [79]. The valence band offset and the conduction band offset of high- κ gate dielectrics should be larger than 1 eV. Liu et al. deposited HfO_xN_y samples on Si(100) by using radio-frequency reactive magnetron sputtering and have demonstrated that valence band offset and conduction band offset of the HfO_xN_y increases with annealing temperature. Table V summarizes the effect of annealing temperature on the band offsets of HfO_xN_y films [80].

TABLE V

Conduction band offsets and valence band offset of HfO_xN_y films: as-deposited, 500 °C, and 800 °C [80]

Annealing temperature	Conduction band offsets (ΔE_c)	Valence band offset (ΔE_v)
as-deposited	0.85	2.46
500 °C	1.20	2.73
800 °C	1.25	2.95

3.2.2. Si-doping

HfSiO_x gate dielectrics, deposited by co-sputtering of hafnium oxide and silicon, in different annealing temperatures were prepared by Lim et al. [81]. In this article, HfSiO_x thin films are thermally more stable than HfO_2 because Si inhibits crystallization of HfO_2 . HfSiO_x films crystallized above 800 °C whereas crystallization of HfO_2 occurred at 500 °C. Six different defects form in HfSiO_x ; oxygen vacancy (V_O^{2+}), hafnium vacancy (V_Hf^{2-} , V_Hf^{4-}),

silicon vacancy (V_{Si}^{2-} , V_{Si}^{4-}), oxygen interstitial (O_i^{2-}), hafnium interstitial (Hf_i^{4+}) and silicon interstitial (Si_i^{4+}). In the presence of V_{Hf}^{4-} , V_{Si}^{4-} , V_O^{2+} defects, the conduction band offset reduces and the leakage current density increases [82].

3.2.3. Al-doping

When Al is added to HfO_2 dielectrics, Hf atom is substituted by an Al atom forming the defect ($Al'_{Hf} = Al_{Hf}^-$) [83]. Interstitial Al defect can be written by

Lu et al. deposited HfO_2 and $HfAlO$ thin films on n -type Si-doped GaAs wafers by atomic layer deposition and stated that effective dielectric constant (κ_{eff}) of HfO_2 increases, while EOT decreases by the addition of Al_2O_3 (Table VI) [84].

3.2.4. Ti-doping

Ti and Hf have the same valence numbers as they both belong to group 4B in the periodic table [78]. The possible defect chemistries can be written according to Eqs. (8)–(11):

Microstructures of HfO_2 , TiO_2 and HfO_2 – TiO_2 films deposited by reactive magnetron sputtering were investigated by Mazur et al. [85]. SEM images of HfO_2 , $(Hf_{0.83}Ti_{0.17})O_x$, $(Hf_{0.72}Ti_{0.28})O_x$, $(Hf_{0.55}Ti_{0.45})O_x$ and TiO_2 thin films are shown in Fig. 4. It can be seen that as the ratio of Ti composition in the thin films increases, surface morphology becomes more homogeneous and smoother. From SEM images, grain sizes of HfO_2 , $(Hf_{0.83}Ti_{0.17})O_x$, $(Hf_{0.72}Ti_{0.28})O_x$, $(Hf_{0.55}Ti_{0.45})O_x$ and TiO_2 thin films can be observed as 20–30 nm, 25–95 nm, 15–25 nm and 30–150 nm, respectively.

$HfTiO$ thin films coated on silicon p -type layer annealed at 400 °C, 500 °C, 600 °C and 700 °C by radio frequency (RF) magnetron co-sputtering were compared by Ye et al. [86]. $HfTiO$ thin film annealed at 600 °C has the lowest leakage current 3.1×10^{-6} A/cm² at –1 V, EOT of 0.8 nm and the highest κ value of 45.9.

TABLE VI

Comparison of effective dielectric permittivity and equivalent oxide thickness for HfO_2 and $HfAlO$ dielectrics [84].

Dielectrics	κ_{eff}	EOT [nm]
HfAlO	13.21	2.63
HfO ₂	3.89	8.28

Fig. 4. SEM images of the surface of: (a) HfO_2 , (b) $(Hf_{0.83}Ti_{0.17})O_x$, (c) $(Hf_{0.72}Ti_{0.28})O_x$, (d) $(Hf_{0.55}Ti_{0.45})O_x$, (e) TiO_2 thin films [85].

3.2.5. Ta-doping

Ta introduction into HfO₂ films has significantly improved crystallization temperature. Yu et al. [87] have stated that crystallization temperature of HfTaON thin films deposited by a dual ion beam sputtering deposition technique (DIBSD) is above 1100 °C, while HfO₂ crystallizes at $\approx$ 400 °C. Ta-doped HfO₂ creates substitutional Ta incorporated in HfO₂ [66] and defect chemistry is likely as follows:

HfTaO thin films with varying Ta composition (20%, 30%, 40%, and 50%) were co-sputtered with different annealing temperatures in N₂ atmosphere by Zhang et al. [88]. The results confirmed that as Ta composition in HfTaO thin films is increased, crystallization temperature increases up to 40 at.% (Table VII).

TABLE VII
Crystallization temperature of HfTaO with various Ta contents [88].

Ta composition [%]	Crystallization temperature [°C]
15	600
20	600
30	800
40	900
43	900
5	800

4. Conclusion

This article has reviewed significant historical developments of high- κ materials and latest progress in Hf-based high- κ gate dielectric fabrication methods and commonly used dopants in HfO₂. Mass-production of 45 nm chips with high- κ /metal gates started in 2007. Then, 22 nm chips, using high- κ gate dielectrics, were demonstrated based on 3D tri-gate transistor architecture in 2011. At the year of 2019, 10 nm processors with high- κ metal gate transistors with 3D structures became commercially available. The processor manufacturers had set a course to decrease the gate length to smaller values in the following years. There is still demand for gate dielectrics with better properties and conquest to find new materials will not be concluded in the next few years.

References

- [1] D. Misra, H. Iwai, H. Wong, *Interface* **14**, 30 (2005).
- [2] M. Salmani-Jelodar, H. Ilatikhameneh, S. Kim, K. Ng, G. Klimeck, *IEEE Trans. Nanotechnol.* **15**, 904 (2016).
- [3] S.C. Lo, Y. Li, J.H. Tsai, *WSEAS Trans. Electron.* **1**, 170 (2004).
- [4] C.F. Shih, C.Y. Hsiao, Y.C. Hsiao, B.C. Chen, C.C. Leu, *Thin Solid Films* **556**, 291 (2014).
- [5] Thermo Scientific, “Characterization of high- κ dielectric materials on silicon using angle resolved XPS”, 2004.
- [6] J. Robertson, *Solid-State Electron.* **49**, 283 (2005).
- [7] A. Navrotsky, S.V. Ushakov, *Materials Fundamentals of Gate Dielectrics*, Eds. A.A. Demkov, A. Navrotsky, USA 2005, p. 56.
- [8] B.R. Kumar, T.S. Rao, *Int. J. Pure Appl. Sci. Technol.* **4**, 105 (2011).
- [9] J.N. Matthews, *Phys. Today* **61**, 25 (2008).
- [10] N. Kazuo, *Dry Etching Technology for Semiconductors*, Springer Int. Publ., Cham 2015, p. 101.
- [11] Intel, **22 nm Technology**.
- [12] C. Auth, C. Allen, A. Blattner, et al., in: *2012 Symp. on VLSI Technology (VLSIT)*, IEEE, 2012, p. 131.
- [13] R.S. Rathore, A.K. Rana, *Superlatt. Microstruct.* **113**, 213 (2018).
- [14] Samsung, *The easy guide to a semiconductor: Why the 10 nm FinFET Process?*.
- [15] Samsung Newsroom, *Samsung Launches Premium Exynos 9 Series Processor Built on the World’s First 10 nm FinFET Process Technology*.
- [16] D. Ha, C. Yang, J. Lee, et al., in: *2017 Symp. on VLSI Technology*, IEEE, 2017, p. T68.
- [17] Samsung Newsroom, *Samsung Electronics Starts Production of EUV-based 7 nm LPP Process*.
- [18] Next Big Future, *Samsung process roadmap 7 nm 2018, 5 nm 2019, 4 nm 2020 and 3 nm 2021*.
- [19] OC3D.NET, *Intel’s 10 nm Ice Lake Processor to Release This Year with Sunny Cove Cores*.
- [20] G.E. Moore, *SPIE Milestone Series MS* **178**, 179 (2004).
- [21] A.I. Kingon, J.P. Maria, S.K. Streiffer, *Nature* **406**, 1032 (2000).
- [22] A.P. Huang, P.K. Chu, Z.C. Yang, in: *Advances in Solid State Circuit Technologies*, Ed. P.K. Chu, InTech, Rijeka 2010, p. 333.
- [23] J. Robertson, *J. Vac. Sci. Technol. B* **18**, 1785 (2000).
- [24] Q. Zeng, A.R. Oganov, A.O. Lyakhov, C. Xie, X. Zhang, J. Zhang, Q. Zhu, B. Wei, I. Grigorenko, L. Zhang, L. Cheng, *Acta Crystallogr. C* **70**, 76 (2014).
- [25] J.P. Locquet, C. Marchiori, M. Sousa, J. Fompeyrine, J. Seo, *J. Appl. Phys.* **100**, 051610 (2006).
- [26] J.C. Pravin, D. Nirmal, P. Prajoun, J. Ajayan, *Physica E* **83**, 95 (2016).
- [27] X.B. Lu, G.H. Shi, J.F. Webb, Z.G. Liu, *Appl. Phys. A* **77**, 481 (2003).
- [28] W. Chen, W. Ren, Y. Zhang, M. Liu, Z.G. Ye, *Ceram. Int.* **41**, S278 (2015).
- [29] H.P. Kumar, S. Vidya, S.S. Kumar, C. Vijayakumar, S. Solomon, J.K. Thomas, *J. Asian Ceram. Soc.* **3**, 64 (2015).
- [30] M.C. Cheynet, S. Pokrant, F.D. Tichelaar, J.L. Rouvière, *J. Appl. Phys.* **101**, 054101 (2007).
- [31] Extremetech, *What is Moore’s law?*, 2015.

- [32] T. Kuroiwa, Y. Tsunemine, T. Horikawa, T. Makita, J. Tanimura, N. Mikami, K. Sato, *Jpn. J. Appl. Phys.* **33**, 5187 (1994).
- [33] R.L. Nigro, E. Schilirò, G. Greco, P. Fiorenza, F. Roccaforte, *Thin Solid Films* **617**, 138 (2016).
- [34] S.J. Lee, S. Baek, *Ceram. Int.* **42**, 9921 (2016).
- [35] Y. Xia, Y.P. Zeng, D. Jiang, *Ceram. Int.* **35**, 1699 (2009).
- [36] J.B. Cheng, A.D. Li, Q.Y. Shao, H.Q. Ling, D. Wu, Y. Wang, Y. Bao, M. Wang, G.Z. Liu, N.B. Ming, *Appl. Surf. Sci.* **233**, 91 (2004).
- [37] M.K. Bera, C.K. Maiti, *Mater. Sci. Semicond. Process.* **9**, 909 (2006).
- [38] C.E. Kim, I. Yun, *Appl. Surf. Sci.* **258**, 3089 (2012).
- [39] M. Houssa, L. Pantisano, L.Å. Ragnarsson, R. Degraeve, T. Schram, G. Pourtois, S.D. Gendt, G. Groeseneken, M.M. Heyns, *Mater. Sci. Eng. R* **51**, 37 (2006).
- [40] A. Salaün, H. Grampeix, J. Buckley, C. Mannequin, C. Vallée, P. Gonon, S. Jeannot, C. Gaumer, M. Gros-Jean, V. Jousseau, *Thin Solid Films* **525**, 20 (2012).
- [41] W. Zheng, K.H. Bowen, J. Li, I. Dabkowska, M. Gutowski, *J. Phys. Chem. A* **109**, 11521 (2005).
- [42] H. Shimizu, T. Nishide, in: *Advances in Crystallization Processes*, Ed. Y. Mastai, InTech, Rijeka 2012, Ch. 13.
- [43] P. Jin, G. He, D. Xiao, J. Gao, M. Liu, J. Lv, Y. Liu, M. Zhang, P. Wang, Z. Sun, *Ceram. Int.* **42**, 6761 (2016).
- [44] S.S. Jiang, G. He, J. Gao, D. Q. Xiao, P. Jin, W.D. Li, J.G. Lv, M. Liu, Y.M. Liu, Z.Q. Sun, *Ceram. Int.* **42**, 11640 (2016).
- [45] F.M. Li, B.C. Bayer, S. Hofmann, J.D. Dutson, S.J. Wakeham, M.J. Thwaites, W.I. Milne, A.J. Flewitt, *Appl. Phys. Lett.* **98**, 252903 (2011).
- [46] Y. Wan, X. Zhou, *RSC Advances* **7**, 7763 (2017).
- [47] J.M. Khoshman, A. Khan, M.E. Kordes, *Surf. Coat. Technol.* **202**, 2500 (2008).
- [48] A.S. Foster, F.L. Gejo, A.L. Shluger, R.M. Nieminen, *Phys. Rev. B* **65**, 174117 (2002).
- [49] K. Suzuki, H. Miura, *Simulat. Semicond. Process. Dev.* **2007**, 165 (2007).
- [50] D. Shin, R. Arróyave, Z.K. Liu, *Calphad* **30**, 375 (2006).
- [51] K.J. Choi, W.C. Shin, J.B. Park, S.G. Yoon, *Integrat. Ferroelectr.* **48**, 13 (2002).
- [52] R. Gupta, R. Rajput, R. Prasher, R. Vaid, *Solid State Sci.* **59**, 7 (2016).
- [53] H. Ikeda, S. Goto, K. Honda, M. Sakashita, A. Sakai, S. Zaima, Y. Yasuda, *Jpn. J. Appl. Phys.* **41**, 2476 (2002).
- [54] G. He, L.Q. Zhu, M. Liu, Q. Fang, L.D. Zhang, *Appl. Surf. Sci.* **253**, 3413 (2007).
- [55] Y. Wang, Z. Lin, X. Cheng, H. Xiao, F. Zhang, S. Zou, *Appl. Surf. Sci.* **228**, 93 (2004).
- [56] Y.K. Lu, X.F. Chen, W. Zhu, R. Gopalkrishnan, *J. Mater. Sci. Mater. Electron.* **17**, 685 (2006).
- [57] A. Vinod, M.S. Rathore, N.S. Rao, *Vacuum* **155**, 339 (2018).
- [58] T. Nishide, S. Honda, M. Matsuura, M. Ide, *Thin Solid Films* **371**, 61 (2000).
- [59] R.R. Goncalves, G. Carturan, L. Zampedri, M. Ferrari, M. Montagna, A. Chiasera, G.C. Righini, S. Pelli, S.J.L. Ribeiro, Y. Messaddeq, *Appl. Phys. Lett.* **81**, 28 (2002).
- [60] K. Suzuki, K. Kato, *J. Am. Ceram. Soc.* **92**, S162 (2009).
- [61] M. Villanueva-Ibanez, C. Le Luyer, O. Marty, J. Mugnier, *Opt. Mater.* **24**, 51 (2003).
- [62] S. Gopalan, S. Ramesh, S. Dutta, V.V. Garbhapu, *IOP Conf. Series Mater. Sci. Eng.* **310**, 012125 (2018).
- [63] S. Sayan, S. Aravamudhan, B.W. Busch, W.H. Schulte, F. Cosandey, G.D. Wilk, T. Gustafsson, E. Garfunkel, *J. Vac. Sci. Technol. A* **20**, 507 (2002).
- [64] J.C. Hackley, T. Gougousi, *Thin Solid Films* **517**, 6576 (2009).
- [65] H. Wang, Y. Wang, J. Feng, C. Ye, B.Y. Wang, H.B. Wang, Q. Li, Y. Jiang, A.P. Huang, Z.S. Xiao, *Appl. Phys. A* **93**, 681 (2008).
- [66] Z. Ying, J. Sun, Z. Hu, W. Yu, N. Xu, J. Wu, *J. Vac. Sci. Technol. A* **30**, 011506 (2012).
- [67] Q. Li, S.J. Wang, W.D. Wang, D.Z. Chi, A.C.H. Huan, C.K. Ong, *J. Electroceram.* **16**, 517 (2006).
- [68] K. Yamamoto, S. Hayashi, M. Niwa, M. Asai, S. Horii, H. Miya, *Appl. Phys. Lett.* **83**, 2229 (2003).
- [69] M. Ramzan, M.F. Wasiq, A.M. Rana, S. Ali, M.Y. Nadeem, *Appl. Surf. Sci.* **283**, 617 (2013).
- [70] K. Cherkaoui, S. Monaghan, M.A. Negara, M. Modreanu, P.K. Hurley, D. O'Connell, S. McDonnell, G. Hughes, S. Wright, R.C. Barklie, P. Bailey, T.C.Q. Noakes, *J. Appl. Phys.* **104**, 064113 (2008).
- [71] Z.J. Yan, R. Xu, Y.Y. Wang, S. Chen, Y.L. Fan, Z.M. Jiang, *Appl. Phys. Lett.* **85**, 85 (2004).
- [72] M. Nath, A. Roy, *Physica B* **482**, 43 (2016).
- [73] C.C. Leu, S.T. Chen, F.K. Liu, *Thin Solid Films* **519**, 5629 (2011).
- [74] J.H. Choi, Y. Mao, J.P. Chang, *Mater. Sci. Eng. R* **72**, 97 (2011).
- [75] A. Jilani, M.S. Abdel-wahab, A.H. Hammad, in: *Modern Technologies for Creating the Thin-Film Systems and Coatings*, Ed. N. Nikitenkov, InTech, 2017.
- [76] S.V. Aurobind, K.P. Amirthalingam, H. Gomathi, *Adv. Coll. Interfac.* **121**, 1 (2006).
- [77] J. Kang, D.Y. Kim, K.J. Chang, *AIP Conf. Proc.* **893**, 263 (2007).
- [78] Z. Yuanyang, W. Jiayu, X. Jianbin, Y. Fei, L. Qi, D. Yuehua, *J. Semicond.* **35**, 042002 (2014).
- [79] G. He, Q. Fang, G.H. Li, J.P. Zhang, L.D. Zhang, *Appl. Surf. Sci.* **253**, 8483 (2007).
- [80] M. Liu, L.D. Zhang, Q. Fang, J.P. Zhang, X.J. Wang, G. He, *J. Phys. D* **42**, 195304 (2009).
- [81] Y.S. Lim, Y.J. Im, S.S. Ha, C.H. Park, M.H. Jang, S.I. Choi, J.I. Park, M. Yi, *J. Soc. Informat. Display* **23**, 384 (2015).
- [82] D. Hai-Kuan, S. Li-Bin, *Chin. Phys. Lett.* **33**, 016101 (2016).

- [83] Q. Li, K.M. Koo, W.M. Lau, P.F. Lee, J.Y. Dai, Z.F. Hou, X.G. Gong, *Appl. Phys. Lett.* **88**, 182903 (2006).
- [84] B. Lu, H. Lv, Yuming Zhang, Yimen Zhang, C. Liu, *Superlatt. Microstruct.* **99**, 54 (2016).
- [85] M. Mazur, D. Kaczmarek, J. Domaradzki, D. Wojcieszak, A. Poniedzialek, *Coatings* **6**, 13 (2016).
- [86] C. Ye, Y. Wang, Jun Zhang, Jieqiong Zhang, H. Wang, Y. Jiang, *Appl. Phys. Lett.* **99**, 182904 (2011).
- [87] T. Yu, C. Jin, X. Yang, Y. Dong, H. Zhang, L. Zhuge, X. Wu, Z. Wu, *Appl. Surf. Sci.* **258**, 2953 (2012).
- [88] M.H. Zhang, S.J. Rhee, C.Y. Kang, C.H. Choi, M.S. Akbar, S.A. Krishnan, T. Lee, I.J. Ok, F. Zhu, H.S. Kim, J.C. Lee, *Appl. Phys. Lett.* **87**, 232901 (2005).