Atomic Layer Deposition and Characterization of Amorphous $\text{Er}_x\text{Ti}_{1-x}\text{O}_y$ Dielectric Ultra-Thin Films

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$\text{Er}_{1-x}\text{Ti}_x\text{O}_y$ dielectric thin films were deposited on Si(100) substrates by atomic layer deposition (ALD) using tris(methylcyclopentadienyl)erbium [(CpMe)₃Er] and tetrakis(diethylamino)titanium [TDEAT] as metal precursors, and O₃ as oxidant. The deposition temperature dependence of both Er₂O₃ and TiO₂ film growths showed the overlapping ALD window of 175–250°C. Compositional tunability of $\text{Er}_{1-x}\text{Ti}_x\text{O}_y$ films was obtained through deposition process control. Carbon and nitrogen impurities in as-deposited films were found to be below X-ray photoelectron spectroscopy detection level. Glancing incidence X-ray diffraction and phase-shifting interferometry results showed that $\text{Er}_x\text{Ti}_{1-x}\text{O}_y$ films with ALD cycle ratios (Er₂O₃/TiO₂) of 1:8 or higher have a good thermal stability and remain amorphous with unchanged surface roughness after post-deposition rapid thermal processing (RTP) at 700°C in O₂. Electrical measurements showed that optimized amorphous $\text{Er}_{1-x}\text{Ti}_x\text{O}_y$ films after RTP exhibited a dielectric constant of ~36, a hysteresis voltage of less than 10 mV, and a leakage current density of 10^{−8} A/cm² at −1 MV/cm; such properties compare favorably with the properties of other reported amorphous titanium-based ternary dielectrics on Si. The sizable reduction of leakage current density of $\text{Er}_{1-x}\text{Ti}_x\text{O}_y$ found in our study suggests that amorphous $\text{Er}_{1-x}\text{Ti}_x\text{O}_y$ thin films are promising future dielectrics in Si integrated circuit technology.

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Thin structures with high dielectric constant (κ) are one of the key components in the future fabrication of semiconductor devices, such as metal oxide semiconductor (MOS) transistors and dynamic random access memories (DRAMs).¹ So far, a variety of high- κ candidates, including HfO₂, ZrO₂, La₂O₃, Y₂O₃, and TiO₂, have been proposed and investigated as replacements of conventional SiO₂ and SiON.¹ From these materials, TiO₂ has been considered to be one of the leading candidates in term of its high dielectric constant, 40 for amorphous or anatase structures and 80 or higher for rutile structure.² However, crystalline TiO₂ often suffers from severe leakage current density (~1 A/cm² at 1 V), because its polycrystalline structure induces a large amount of grain boundaries, which serve as high leakage and Si dopants (i.e., B or P) diffusion paths.^{2–5} In addition, structural transitions and multiphase crystalline TiO₂ yield variable electrical properties, such as uneven capacitance values and leakage current characteristics among different regions.⁴ Therefore, stabilization of TiO₂ in its amorphous state throughout necessary thermal processes has been regarded as one of the challenges to achieve a high permittivity thin film without sacrificing its leakage current characteristics and reliability.^{2,5}

An attractive approach to suppress crystallization of TiO₂ is doping it with other high- κ metal oxides, such as Al₂O₃, HfO₂, ZrO₂, Ta₂O₅ and Ln₂O₃, forming thermally stable amorphous high- κ ternary oxides.^{2,5–9} For instance, a recent study of Al-doped TiO₂ dielectric showed that the incorporation of Al could mostly result in amorphous ternary oxide throughout necessary annealing processes, thereby reducing the leakage current density of anatase TiO₂ (10¹ A/cm² at 0.16 MV/cm) on a TaN electrode.² However, it was reported that optimized AlTiO_x dielectrics were found to be incompatible with Si electrodes and yielded a leakage current density of 10^{−4} A/cm² at 0.16 MV/cm.² Jeon et al. reported that addition of praseodymium into titanium oxide films using *E-beam* evaporation made it possible to achieve amorphous films with a dielectric constant of ~23 and a leakage current density of ~10^{−5} A/cm² at −2 MV/cm on Si.⁷ Among other lanthanide oxides, erbium oxide, as a novel high- κ candidate, is of particular interest due to its large conduction band offset to Si (3.5 eV), low leakage current density (10^{−8} A/cm² at 1 V), and a moderate dielectric constant (10–14).^{10,11} In addition, studies of Er₂O₃ thin films showed a low fixed charge density and minimal interdiffusion between Er₂O₃ and Si substrate when used in metal-insulator-silicon (MIS) gate stacks.¹² Thus, Er₂O₃ could be a promising dopant of TiO₂

films, especially for the reduction in leakage current density by several orders of magnitude.

A challenge in the implementation of amorphous Ln-doped TiO₂ dielectric films is the development of a suitable route for thin film deposition; a few techniques such as co-precipitation,¹³ *E-beam* evaporation,⁷ and magnetron sputtering have been applied.¹⁴ In cutting-edge micro/nanoelectronics fabrication, atomic layer deposition (ALD) has been identified as one of the preferred means of fabricating nanoscale features in the semiconductor industry, because it offers distinct advantages and meets demanding requirements such as precise thickness control at the required dimensions within MOS devices and conformal coverage in the deep trenches of memory cells.¹⁵ In addition, ALD may enable composition tunability in the resulting materials, especially for ternary materials, which is important in determining structural, thermal and electrical properties of resulting dielectric films.

In this study, we report on the doping of TiO₂ with Er₂O₃ using ALD to form Si-compatible amorphous $\text{Er}_x\text{Ti}_{1-x}\text{O}_y$ dielectrics with tunable content of Er. Tris(methylcyclopentadienyl)erbium [(CpMe)₃Er] and tetrakis(diethylamino) titanium [TDEAT] are used in the deposition of these films. $\text{Er}_x\text{Ti}_{1-x}\text{O}_y$ films are analyzed and discussed in terms of impurity level, interfacial layer, structure, and surface morphology in order to investigate the effect of Er incorporation on the properties of as-deposited and post-deposition rapid thermal processing (RTP)-treated films. Furthermore, electrical measurements on $\text{Er}_x\text{Ti}_{1-x}\text{O}_y$ films are performed before and after RTP treatment in order to develop optimized Si-compatible $\text{Er}_x\text{Ti}_{1-x}\text{O}_y$ dielectrics with ultra-low leakage current, negligible hysteresis voltage, and high permittivity. After RTP treatment, the leakage current density of $\text{Er}_x\text{Ti}_{1-x}\text{O}_y$ dielectrics on Si (10^{−8} A/cm² at −1 MV/cm), for example, is found to be superior to those reported for amorphous thin dielectrics, such as AlTiO_x (125 nm)/Al₂O₃ (4 nm) ($J = 10^{-4}$ A/cm² on Si or 10^{−7} A/cm² on TaN at 0.16 MV/cm),² TaTiO ($J = 10^{-3}$ A/cm² at 1 MV/cm on TiN),⁹ and Zr_xTi_{1-x}O₂ ($J = 10^{-5}$ A/cm² at 1 MV/cm on RuO₂).⁵

Experimental

$\text{Er}_x\text{Ti}_{1-x}\text{O}_y$ thin films made use of (CpMe)₃Er and TDEAT as metal precursors and ozone as oxidant (1000 ppm ozone in oxygen). Prior to deposition, Si (15 mm × 20 mm) samples were cleaned with the Radio Corporation of America (RCA) standard cleaning (SC-1) procedure to remove organic contaminants, followed by a 1% hydrofluoric acid dip for 20 s to reduce native oxide down to ~0.6 nm on Si surface.

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Each of these two steps was followed by thorough deionized water rinse and drying in N_2 . After cleaning, Si substrates were immediately loaded into a custom designed hot wall ALD reactor for deposition. Both metal precursors were kept in stainless steel bubblers; during deposition, the $(CpMe)_3Er$ bubbler was maintained at $100^\circ C$ and the TDEAT one at $65^\circ C$.

Film thickness was measured with a spectral ellipsometer (Model M-44, J. A. Woollam Co.); for each thickness determination, three measurements across the entire deposition area were carried out with mean values representing film thickness and standard deviation indicating thickness variation. Chemical bonding states of $Er_xTi_{1-x}O_y$ films were probed with a high resolution XPS (Kratos AXIS-165, Kratos Analytical Ltd.) equipped with a monochromatic Al $K\alpha$ (1486.6 eV) X-ray source operating at 15 kV and 10 mA. High resolution XPS spectra of the elements-of-interest were collected using pass energy of 20 eV, step size of 0.1 eV, and dwell time of 200 ms. The Carbon 1s line at 285 eV was used to calibrate the binding-energy scale of the XPS spectra. The analyses of $Er_xTi_{1-x}O_y$ films were performed through XPS spectral peak-fitting, where peaks were subtracted from Shirley-type backgrounds and deconvoluted using Gaussian-Lorentzian peak shape functions. For studies on thermally induced changes at the interface, surface roughness, and electrical properties, the ALD films were annealed in an RTP furnace (RTP-600S, Modular Process Technology Co.) at $700^\circ C$ for 30 s in O_2 at 1 atm. The bulk composition of the resulting films was investigated using Rutherford back scattering (RBS) spectroscopy with a general ionex tandemron accelerator (Model 5510, General Ionex Co.) employing 2 MeV He^+ particles. An X-ray diffractometer (X'pert, PANalytical, BN Co.) was used to obtain glancing incidence X-ray diffraction (GIXRD) patterns of as-deposited and RTP-treated films. The overall diffraction angle (2θ) resolution was 0.15° . GIXRD diffractograms were collected at an incident angle of 1° to enhance diffraction sensitivity within the film and to minimize interference from the single crystal Si (100) substrate. The crystalline features were identified using the International Center for Diffraction Data (ICDD) database of diffraction pattern Powder Diffraction Files (PDF).

Current density-voltage (J-V) and capacitance-voltage (C-V) characterizations were performed using an Agilent 4980 LCR meter equipped with a mercury probe station (Model 802 B, Materials Development Co.). The C-V characterizations were carried out at 10 kHz. The variation of C-V measurements was less than 2%. The metal-oxide-semiconductor capacitor formed with the mercury probe had an area of 0.5 mm^2 . The dielectric constant of high- κ films was calculated from the capacitance-in-series model (high- κ /interfacial film) using a dielectric constant of 3.9 for the interfacial oxide.³ The interface-thickness of RTP-treated films was $2.7 \pm 0.2\text{ nm}$ as measured with spectral ellipsometry and transmission electron microscopy. Surface morphology of as-deposited and RTP-treated films was investigated using a noncontact optical profiler system (Wyko NT3300, Veeco Instrument Inc.) in the phase-shifting interferometry (PSI) mode with a vertical resolution of 0.1 nm. PSI is based on the interference of light to produce high-precision images of surfaces.

Results and Discussion

ALD temperature window and growth of $Er_xTi_{1-x}O_y$ films.— A sufficient overlap of ALD temperature windows of the constituent binary processes is desirable for the ALD of ternary thin films; this overlap could effectively improve the reproducibility of the ternary film growth. Figure 1 shows the temperature dependence of growth rates of both Er_2O_3 and TiO_2 . At low temperatures, high growth rates that decrease with increasing substrate temperature were observed for both oxide thin films; these growth rates indicate a non self-limiting growth behavior likely resulting from multilayer condensation of the precursor during precursor pulsing. At high temperatures, the low growth rates of Er_2O_3 could be attributed to lower adsorption of $(CpMe)_3Er$ on the reaction surface, whereas the rapid increase in the growth rate of TiO_2 was attributed to thermal decomposition of TDEAT at temperature higher than $250^\circ C$.¹⁶ The region where the growth rate is

Figure 1. Dependence of growth rates of Er_2O_3 and TiO_2 films on ALD reactor temperature. The Er and Ti precursors were kept at 100 and $65^\circ C$, respectively. The error bars indicate film uniformity across the sample.

found to be independent of deposition temperature is taken as the ALD temperature window for each oxide process. In this system, a sufficiently overlapping temperature window of the binary oxide processes was found to be between 175 and $250^\circ C$; this common window offers a suitable temperature range for depositing $Er_xTi_{1-x}O_y$ films. Therefore, the deposition temperature of each metal oxide as well as of $Er_xTi_{1-x}O_y$ composite films in this study was maintained at $245^\circ C$.

Figure 2 shows the dependence of Er_2O_3 , TiO_2 , and $Er_xTi_{1-x}O_y$ films thicknesses on the total number of ALD cycles, and this dependence corroborates the precise thickness control of self-limiting ALD processes. For the ALD of each single-component oxide, linear regression analyses yield growth rates of 0.12 nm/cycle for Er_2O_3 and 0.047 nm/cycle for TiO_2 . The growth rate of Er_2O_3 is found to be at least two times higher than that in earlier ALD studies using $Er(thd)_3$ and $Er(tBu_2amd)_3$ with O_3 as oxidant.^{17,18} On the other hand, the growth rate of TiO_2 is slightly lower than that obtained in our earlier study using the same precursor and moisture as oxidant in a different

Figure 2. Thicknesses of Er_2O_3 and TiO_2 films as functions of ALD cycle number (main). Thicknesses of $Er_xTi_{1-x}O_y$ films with ALDCR (i.e., $Er_2O_3:TiO_2$) of 1:1 and 1:3 are shown as a function of the number of cycles in the inset. All films were deposited at $245^\circ C$. Other ALD conditions were the same as those in Fig. 1.

Figure 3. (a) $\text{Er}_x\text{Ti}_{1-x}\text{O}_y$ (34 nm-thick) film composition evaluated using RBS as a function of normalized cycle ratio of $\text{Er}_2\text{O}_3/(\text{Er}_2\text{O}_3+\text{TiO}_2)$. (b) RBS spectrum of as-deposited $\text{Er}_x\text{Ti}_{1-x}\text{O}_y$ film with an ALDCR of 1:3. Other ALD conditions were the same as those in Fig. 2.

ALD system,⁶ but higher than that reported with other titanium precursors such as titanium isopropoxide (TTIP) and TiCl_4 , using water or even oxygen plasma as oxidant.^{19,20} Such findings suggest relatively high reactivity of TDEAT with oxidants (i.e., H_2O or O_3) on silicon in our ALD reactors.

The growth of $\text{Er}_x\text{Ti}_{1-x}\text{O}_y$ films shows a linear dependence of the film thickness on the number of ALD cycles (inset of Fig. 2). Moreover, the average growth rate is seen to increase with the ALD cycle ratio (ALDCR) of $\text{Er}_2\text{O}_3/\text{TiO}_2$; $\text{Er}_x\text{Ti}_{1-x}\text{O}_y$ films with ALDCR of 1:3 and 1:1 yield growth rates of 0.051 and 0.064 nm/cycle, respectively. The self-limiting feature of the ALD processes in this work is also represented by the high degree of uniformity of Er_2O_3 , TiO_2 , and $\text{Er}_x\text{Ti}_{1-x}\text{O}_y$ film thicknesses across the entire deposition area (Fig. 2).

Composition tunability - impurities.— In order to study composition tunability of the atomic layer deposited $\text{Er}_x\text{Ti}_{1-x}\text{O}_y$ films, a series of depositions was carried out with different ALD cycle ratios. For example, for a normalized cycle ratio $[\text{Er}_2\text{O}_3/(\text{TiO}_2+\text{Er}_2\text{O}_3)]$ of 0.2, one cycle of Er_2O_3 deposition alternated with four cycles of TiO_2 deposition. Figure 3 shows the effect of normalized cycle ratio $[\text{Er}_2\text{O}_3/(\text{TiO}_2+\text{Er}_2\text{O}_3)]$ on atomic composition $[\text{Er}/(\text{Ti}+\text{Er})]$ of 34 nm-thick as-deposited $\text{Er}_x\text{Ti}_{1-x}\text{O}_y$ films, as determined from quantitative analyses of RBS spectra. The atomic ratio of $\text{Er}/(\text{Ti}+\text{Er})$ in $\text{Er}_x\text{Ti}_{1-x}\text{O}_y$ films is found to monotonically increase almost linearly

with increasing normalized cycle ratio $[\text{Er}_2\text{O}_3/(\text{TiO}_2+\text{Er}_2\text{O}_3)]$. This shows that the Er content in the resulting films can be effectively controlled by varying the ALDCR of Er_2O_3 and TiO_2 . Similar effective atomic composition tunability was also reported in earlier studies with the ALD of other composite metal oxides, such as Y_2O_3 -doped HfO_2 and HfO_2 -doped TiO_2 .^{6,21}

For MOS and memory applications, impurities (e.g., C or Cl) in gate dielectric films are undesirable; they can be incorporated during deposition and often cause degradation of electrical performance, especially because of increased electronic trap centers and defects.²² Also, it was reported that carbon contamination could notably increase crystallization temperature of oxide films.⁸ The impurity content of as-deposited films can be generally minimized with optimization of deposition conditions used, such as deposition temperature, operating pressure, and nature of precursor(s). Therefore, it is necessary to investigate the level of impurities in $\text{Er}_x\text{Ti}_{1-x}\text{O}_y$ films formed with TDEAT/ O_3 and $(\text{CpMe})_3\text{Er}/\text{O}_3$ in our ALD studies. Figure 3b shows an RBS spectrum from a 34 nm-thick $\text{Er}_x\text{Ti}_{1-x}\text{O}_y$ film with ALDCR of 1:3. The RBS reveals that there is no detectable nitrogen and carbon contamination in the film, which is corroborated by surface-sensitive XPS analyses (Fig. 4). No peaks are observed in the XPS spectrum of N 1s (Fig. 4a). After sputtering the film surface with ~ 200 nA Ar^+ beam for 10 min, the amount of surface carbon contamination seems to be at the XPS detection limit, i.e., less than 0.5 atom% (Fig. 4b).

Figure 4. N 1s and C 1s XP spectra of $\text{Er}_x\text{Ti}_{1-x}\text{O}_y$ film with an ALD cycle ratio of $\text{Er}_2\text{O}_3/\text{TiO}_2 = 1:3$. XP spectra were collected at 90° take-off angle. C 1s spectra were collected before and after sputtering the surface using ~ 200 nA Ar^+ beam for 10 min. Other ALD conditions were the same as those in Fig. 2.

Figure 5. Er 4d (a), Ti 2p (b), O 1s (c), and Si 2p (d) core level XPS spectra of as-deposited and RTP-treated 3.5 nm-thick $\text{Er}_x\text{Ti}_{1-x}\text{O}_y$ films with ALDCR of 1:3. The film was rapid thermal annealed at 700°C in O_2 for 30 s. Other ALD conditions were the same as those in Fig. 2.

Such a low impurity level is in agreement with earlier studies of atomic layer deposited Er_2O_3 and chemical vapor deposited TiO_2 using $(\text{CpMe})_3\text{Er}/\text{H}_2\text{O}$ and TDEAT/ O_2 processes, respectively.^{8,11}

$\text{Er}_x\text{Ti}_{1-x}\text{O}_y/\text{Si}$ interface.— The XPS spectra of 3.5 nm-thick $\text{Er}_x\text{Ti}_{1-x}\text{O}_y$ films with ALDCR of 1:3 are shown in Fig. 5. The XPS spectra were collected at a take-off angle of 90° in order to obtain information about the $\text{Er}_x\text{Ti}_{1-x}\text{O}_y/\text{Si}$ interfacial region. The $\text{Er}_x\text{Ti}_{1-x}\text{O}_y$ films deposited with different ALD cycle ratios generally have similar peak shapes and locations of the XPS spectral features. The Er 4d core-level spectra of as-deposited and RTP-treated $\text{Er}_x\text{Ti}_{1-x}\text{O}_y$ films show the same dominant feature centered at 168.8 eV (Fig. 5a), corresponding to the signature peak of Er^{3+} .¹⁰ The small feature at the higher binding energy is attributed to the formation of Er silicate at the interface during deposition. Peaks indicative of erbium silicide at the lower binding energy of 168 eV are not observed. The Ti 2p core-level spectra of $\text{Er}_x\text{Ti}_{1-x}\text{O}_y$ films before and after post-deposition RTP consist of two peaks assigned to $\text{Ti } 2p_{1/2}$ and $\text{Ti } 2p_{3/2}$ (Fig. 5b), in agreement with the oxidation state of Ti^{4+} .⁶ No feature is found at lower binding energies than 453.9 eV; therefore, no titanium silicide is formed.

In order to further analyze the effect of post-deposition RTP on the $\text{Er}_x\text{Ti}_{1-x}\text{O}_y/\text{Si}$ interface, O 1s and Si 2p core-level spectra of as-deposited and RTP-treated films are shown in Figs. 5c and 5d, respectively. The O 1s spectrum of the as-deposited film (Fig. 5c, bottom) could be deconvoluted into three peaks, which are attributed to different chemical bonding states of the $\text{Er}_x\text{Ti}_{1-x}\text{O}_y/\text{Si}$ system: the dominant one at 530.3 eV is consistent with an M-O-M binding state (M refers to Er or Ti), while the two shoulder peaks located at 531.2 and 532.4 eV are assigned to M-O-Si and O-Si binding states of silicate and SiO_2 , respectively.⁶ Therefore, after ALD, the species at the $\text{Er}_x\text{Ti}_{1-x}\text{O}_y/\text{Si}$ interface seems to be silicate and SiO_2 . Following the RTP treatment at 700°C, the O-Si peak at 532.4 eV is found to increase in intensity (Fig. 5c), which suggests increased formation of SiO_2 at the interface. This finding is corroborated by analyses of the Si 2p spectra (Fig. 5d) that show two main peaks at the binding energies of 99.3 and 99.8 eV (attributed to the Si substrate) along with two features at 102.2 and 103.1 eV assigned to silicate and SiO_2 , respectively.⁶ The Si 2p spectra show that the SiO_2 peak intensity of the RTP-treated film is higher than that of the as-deposited film, in agreement with increased formation of SiO_2 at the $\text{Er}_x\text{Ti}_{1-x}\text{O}_y/\text{Si}$ interface after the post-deposition RTP used.

Effect of rapid thermal processing on the $\text{Er}_x\text{Ti}_{1-x}\text{O}_y$ film structure.— The structure of dielectric films is important in determining their electrical characteristics, especially leakage current density. For example, Kwon et al. reported TiO_2 film suffers from serious leakage current ($\sim 0.1 \text{ A/cm}^2$ at 1 V) after post-deposition annealing at 500°C, which was attributed to a large amount of grain boundaries

induced by film crystallization.⁵ In the present study, structures of TiO_2 and $\text{Er}_x\text{Ti}_{1-x}\text{O}_y$ films before and after post-deposition RTP were investigated using GIXRD (Fig. 6). All films were 34 nm-thick as measured with spectroscopic ellipsometry. The corresponding lattice structures of diffraction peaks were identified and labeled as indicated in Fig. 6.

As-deposited TiO_2 films show a trace presence of a diffraction feature at 25°, which corresponds to anatase (101) and therefore suggests onset of TiO_2 film crystallization at the deposition temperature of 245°C. A similar onset of TiO_2 crystallization temperature in the anatase phase was observed and reported in an earlier ALD study utilizing the $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4/\text{H}_2\text{O}$ process on Si substrates.²³ On the other hand, the pure amorphous structure of TiO_2 film deposited at a lower temperature (i.e., 200°C) was obtained in our earlier study using TDEAT with moisture as oxidant, and that work indeed suggested a higher onset crystallization temperature than 200°C for TiO_2 on Si.⁶ After RTP at 700°C in O_2 , a sharp increase of the diffraction peak of TiO_2 (101) at 25° was observed (Fig. 6) along with the appearance of

Figure 6. GIXRD patterns of as-deposited and RTP-treated TiO_2 films as well as of RTP-treated $\text{Er}_x\text{Ti}_{1-x}\text{O}_y$ with ALDCR of 1:12 (main); diffractograms of RTP-treated amorphous $\text{Er}_x\text{Ti}_{1-x}\text{O}_y$ films with ALDCR of 1:8 or higher (inset). GIXRD characterizations were collected at an incident angle of 1°. All deposition and RTP treatment conditions were the same with those in Fig. 5. Anatase TiO_2 reference: PDF Card No. 00-021-1272.

features at 48.1, 53.9, and 55° that were assigned to (200), (105), and (211), respectively; these are indicative of anatase TiO₂. The absence of rutile peaks in the XRD pattern suggests no phase transition to rutile during the post-deposition RTP used. This is in agreement with earlier studies on TiO₂ films grown with TDEAT/H₂O or TTIP/H₂O ALD processes and annealed in N₂,^{6,23} but it is in contrast to the presence of the TiO₂ rutile phase in films deposited from the TDEAT/O₂ chemical vapor deposition (CVD) process followed by post-deposition annealing at the same temperature in Ar.⁸

All as-deposited Er-doped TiO₂ films with the ALDCR used were found to be amorphous, since no features were found in their diffraction patterns (not shown). After the post-deposition RTP, a weak diffraction pattern corresponding to the anatase structure emerges in the resulting Er_xTi_{1-x}O_y film deposited with ALDCR of 1:12 (Fig. 6 main), representing a likely onset of crystallization under the annealing condition used. On the contrary, RTP-treated Er_xTi_{1-x}O_y films deposited with ALDCR of 1:8, 1:5, 1:3, and 1:1 remain amorphous (Fig. 6 inset), and this result is attributed to the breaking of the originally crystalline structure of TiO₂ due to a sufficient dosage of Er. Similar annealing behavior of amorphous ternary gate oxides was observed in previous ALD studies of Hf-doped TiO₂, Zr-doped TiO₂, and Al-doped TiO₂ films.^{5,6,8} Such a good thermal stability of amorphous Ti-based ternary gate oxides is mostly attributed to the incorporation of ions with radii much larger or smaller than Ti, and these impurity atoms could significantly distort the original TiO₂ structure and enhance the entropy for the crystallization process.

Surface morphology and roughness.— The surface morphology and roughness of dielectric films are significant for CMOS applications, for example, because uneven surface morphology could lead to variable electrical properties at different regions.⁴ Also, changes in surface roughness often reveal changes in the underlying structure.⁶ In this study, the surface roughness of films was investigated using the PSI mode of an optical surface profiler. Figure 7a shows the root-mean-square (rms) roughness of 34 nm-thick TiO₂ and Er_{1-x}Ti_xO_y films for various ALDCR measured before and after RTP at 700°C in O₂. For as-deposited films, all Er_{1-x}Ti_xO_y films are found to have rms roughness of ~0.4 nm. The TiO₂ film shows a higher rms roughness of ~0.6 nm, which coincides with the onset of TiO₂ film crystallization at the ALD conditions used (Fig. 6).⁶ After RTP treatment, the rms roughnesses of Er_{1-x}Ti_xO_y films with ALDCR of 1:8, 1:5, 1:3, and 1:1 are found to barely increase (Fig. 7a), suggesting good thermal stability of the underlying structure; the slight increase in rms roughness of Er_{1-x}Ti_xO_y films with ALDCR of 1:12 is likely due to the presence of crystalline phase (Fig. 6). Figures 7b and 7c show the PSI images of RTP-treated amorphous Er_{1-x}Ti_xO_y film and crystalline TiO₂ film, respectively; the latter apparently shows a rougher surface with visible clusters on its surface. The rms roughness of post-deposition RTP TiO₂ films, 1.1 nm, is found to be double that of as-deposited films, and such a sharp increase in rms roughness is often accompanied with structural phase change (Fig. 6).⁶ The rms roughness of the resulting anatase TiO₂ film is similar to that of 30 nm-thick anatase TiO₂ film deposited with the TDEAT/H₂O process, but higher than that of amorphous TiO₂ film (rms = 0.26) deposited at 200°C.⁶ Thus, changes in surface morphology and rms roughness are found to relate to structural transitions (e.g., from amorphous to anatase), suggesting that the incorporation of Er into TiO₂ film could suppress crystallization and prevent surface roughening during annealing. An earlier study of TiO₂ showed a much higher rms roughness (~4 nm) for 30 nm-thick TiO₂ deposited by CVD process using TTIP as the metal precursor at 300°C,⁸ and this indicates the deposition process itself could be another contributing factor to surface roughness.

Electrical characteristics.— The C-V measurement of Er_{1-x}Ti_xO_y films was performed before and after RTP treatment over the voltage range of -3 to +3 V. The electrical parameters of the resulting films were extracted from the C-V data.⁴ Figure 8 (inset) shows the hysteretic behavior of Er_{1-x}Ti_xO_y films deposited with ALD cycle ratio of Er₂O₃/TiO₂ = 1:1. Prior to RTP, the as-deposited Er_{1-x}Ti_xO_y

Figure 7. Surface rms roughnesses of as-deposited and RTP-treated TiO₂ and Er_xTi_{1-x}O_y films as measured by PSI (a); PSI images of RTP-treated Er_{1-x}Ti_xO_y film with ALDCR of 1:3 (b) and TiO₂ film (c). Er_xTi_{1-x}O_y films were deposited with different ALDCR of 1:12, 1:8, 1:5, 1:3, and 1:1 labeled in (a). All deposition and RTP treatment conditions were the same as those in Fig. 5.

film exhibited an instability in the flatband voltage (i.e., ΔV_{fb} = 1500 mV) and a large hysteresis in the counterclockwise direction. Such hysteretic behavior in the C-V measurements of an MOS capacitor is indicative of the presence of trapped charges in the gate oxide, and this is mostly related to oxygen vacancies or interstitial oxygen defects formed during deposition.^{4,24} Also, the significant shift of flatband voltage toward positive bias suggests a considerable amount of negative charges trapped in the as-deposited film, which is consistent with the high trapped charge density ($6.9 \times 10^{12} \text{ cm}^{-2}$) extracted from the C-V data. Since the large hysteresis of as-deposited Er_{1-x}Ti_xO_y film still hampers its use for high- κ applications, additional treatment could be necessary to improve the C-V characteristics of the film.

Based on earlier studies of gate oxides, it is suggested that a large bulk density of defects and trapped charges can be reduced by subjecting gate oxides to appropriate annealing treatments.^{3,4} For instance, Lehnert et al. recently reported that annealing treatment in O₃ at a temperature lower than 400°C could reduce oxygen vacancy defects in TiO₂ dielectrics.² In our study, as-deposited Er_{1-x}Ti_xO_y films were

Figure 8. C-V hysteretic behavior for as-deposited and RTP-treated $\text{Er}_x\text{Ti}_{1-x}\text{O}_y$ films with ALCR of 1:1 (inset), and the dielectric constant of RTP-treated $\text{Er}_x\text{Ti}_{1-x}\text{O}_y$ films as a function of ALDCR (main). The thickness of films is 34 nm. All other deposition and RTP treatment conditions were the same as those in Fig. 5.

subjected to post-deposition RTP in O_2 at 700°C for 30 s in order to passivate defects and improve C-V characteristics. As seen in Fig. 8 (inset), the RTP-treated $\text{Er}_{1-x}\text{Ti}_x\text{O}_y$ film exhibits a remarkably small hysteresis (i.e., $\Delta V_{\text{fb}} = 5$ mV), a flatband voltage at -0.26 V, and a lower trapped charge density ($6 \times 10^{11} \text{ cm}^{-2}$), indicating that the RTP treatment used can effectively lead to significant improvements in the C-V characteristics of such structures.

The effect of Er incorporation on the permittivity value of TiO_2 -based film at different ALDCR is shown in Fig. 8 (main). Prior to these measurements, all $\text{Er}_{1-x}\text{Ti}_x\text{O}_y$ dielectrics were treated with RTP to enhance electrical properties. As the ALDCR increased from 1:12 to 1:1, the dielectric constant of resulting films is found to continuously decrease from 45 to 28, which can be attributed to the increasing content of Er_2O_3 (Fig. 3). The κ value of amorphous $\text{Er}_{1-x}\text{Ti}_x\text{O}_y$ films is found to be comparable with that of mostly amorphous $\text{AlTiO}_x/\text{Al}_2\text{O}_3$ films,² and higher than the highest permittivity ($\kappa = 30$) of amorphous HfO_2 reported recently.²⁵ However, the dielectric constant of amorphous $\text{Er}_{1-x}\text{Ti}_x\text{O}_y$ films is lower than that of pure TiO_2 ($\kappa = 40\text{--}110$) crystallized in the tetragonal structure (i.e., anatase or rutile). The relatively higher κ value of $\text{Er}_{1-x}\text{Ti}_x\text{O}_y$ film with ALDCR of 1:12 can be attributed to the presence of some tetragonal crystalline phase in the bulk film. For high- κ applications, it is desirable for the gate oxide to remain amorphous throughout implemented or necessary annealing process(es), because amorphous films often exhibit isotropic electrical properties and can be deposited by different techniques. On the contrary, grain size and orientation changes throughout a polycrystalline film can cause large variations in its κ value. Furthermore, grain boundaries in crystalline phases often serve as high-leakage paths (planar defects), leading to inferior leakage characteristics (also discussed later).

Figure 9 shows electrical characteristics of RTP-treated $\text{Er}_{1-x}\text{Ti}_x\text{O}_y$ films, i.e., trapped charge density, hysteresis voltage, and flatband voltage. The RTP-treated $\text{Er}_{1-x}\text{Ti}_x\text{O}_y$ films with ALDCR of 1:8 or higher are found to exhibit low trapped charge densities, on the order of 10^{-11} cm^{-2} , and small hysteresis voltages, less than 10 mV. The trapped charge density of RTP-treated $\text{Er}_{1-x}\text{Ti}_x\text{O}_y$ films is seen to be an order of magnitude lower than that of Y-doped HfO_2 film.²⁶ On the other hand, the RTP-treated $\text{Er}_{1-x}\text{Ti}_x\text{O}_y$ film with the lower ALDCR of 1:12 shows a notably higher trapped charge density ($\sim 10^{12} \text{ cm}^{-2}$); this could be connected to the phase transition discussed earlier (Fig. 6) and the increased presence of defects in the resulting film.

The leakage current density of crystalline TiO_2 dielectric films was investigated previously, and a large value, i.e., 1 A/cm^2 at 1 V, was reported.² In this work, as-deposited TiO_2 films are found to exhibit a leakage current density of 10^{-7} A/cm^2 at -1 V, i.e., less than 10^{-4} A/cm^2 at -1 MV/cm (Fig. 10). This is attributed to the

Figure 9. Trapped charge density (a), hysteresis voltage (b), and flatband voltage (c) of RTP-treated 34 nm-thick $\text{Er}_x\text{Ti}_{1-x}\text{O}_y$ films deposited with ALDCR of 1:12, 1:8, 1:5, 1:3, and 1:1. All other deposition and RTP treatment conditions were the same as those in Fig. 5.

Figure 10. J-V characteristics of as-deposited TiO_2 and $\text{Er}_x\text{Ti}_{1-x}\text{O}_y$ films with ALDCR of 1:8 and 1:1 as marked. The inset shows the leakage current density of films measured at -1 MV/cm . The thickness of films is 34 nm. All other deposition and RTP treatment conditions were the same as those in Fig. 5.

mostly amorphous phase of the as-deposited film, since crystalline structure can induce undesired grain boundaries, serving as planar defects and high-leakage paths. A leakage reduction was achieved by incorporation of Er_2O_3 into TiO_2 , and this was likely due to the absence of grain-boundary-induced defects in its amorphous phase. Also, the TiO_2 -Si conduction-band offset (1 eV) is lower than that of Er_2O_3 -Si (3.5 eV).²⁷ The leakage current density in $\text{Er}_{1-x}\text{Ti}_x\text{O}_y$ films is therefore seen to decrease with increasing Er content (Fig. 10).

The effect of RTP treatment on the J-V characteristics of both TiO_2 and $\text{Er}_{1-x}\text{Ti}_x\text{O}_y$ films was also investigated and our results are shown in Fig. 11. The RTP-treated TiO_2 film shows a leakage current density on the order of 10^{-2} A/cm^2 at -1 MV/cm . Such a considerable leakage degradation can be attributed to a wide distribution of grain boundaries in TiO_2 arising from a phase transition, e.g., from mostly amorphous into anatase structure. A similar tendency was observed in

Figure 11. J-V characteristics of RTP-treated TiO_2 and $\text{Er}_x\text{Ti}_{1-x}\text{O}_y$ films deposited with ALDCR of 1:12, 1:8, 1:5, 1:3, and 1:1. The inset shows the leakage current density of films measured at -1 MV/cm . The thickness of films is 34 nm. All deposition and RTP treatment conditions were the same as those in Fig. 5.

earlier ALD studies of TiO_2 , in which post-deposition annealed TiO_2 films were reported to have worse leakage characteristics resulting from crystallization.^{2,5} In this study, the leakage current density of RTP-treated TiO_2 with anatase structure is one order of magnitude lower than that of rutile TiO_2 reported earlier (10^{-1} A/cm^2),⁵ and this is likely related to a higher bandgap of anatase TiO_2 (3.2 eV) than that of rutile TiO_2 (3.0 eV). Among RTP-treated $\text{Er}_{1-x}\text{Ti}_x\text{O}_y$ films with different ALDCR, the film with an ALDCR of 1:12 is found to exhibit a leakage current density of 10^{-2} A/cm^2 at -1 MV/cm , which is at least 5 orders of magnitude higher than that of films with ALDCR of 1:8 or higher. This is in agreement with our GIXRD results, which showed the presence of anatase phase in the RTP-treated $\text{Er}_{1-x}\text{Ti}_x\text{O}_y$ film with ALDCR of 1:12. The significant improvement in leakage reduction obtained for RTP-treated amorphous $\text{Er}_{1-x}\text{Ti}_x\text{O}_y$ films with ALDCR of 1:8 or higher could be attributed to two factors: first, the post-deposition RTP could saturate oxygen vacancies and fix related defects, which are major source of charges and can act as leakage paths in metal oxides;³ and second, as the GIXRD results showed, the RTP-treated $\text{Er}_{1-x}\text{Ti}_x\text{O}_y$ films with ALDCR of 1:8 or higher can effectively suppress crystallization and remain amorphous (Fig. 6) that in turn lack planar defects, such as grain boundaries.

The leakage current density of amorphous $\text{Er}_{1-x}\text{Ti}_x\text{O}_y$ films (10^{-8} A/cm^2 at -1 MV/cm) is one order of magnitude lower than 125 nm-thick amorphous AlTiO_x film deposited on TaN with a 4 nm-thick Al_2O_3 interlayer.² Yet, the $\text{AlTiO}_x/\text{Al}_2\text{O}_3$ film was reported to be incompatible with Si, showing a much higher leakage current density of $5 \times 10^{-4} \text{ A/cm}^2$ at 0.16 MV/cm on a Si electrode. An amorphous Ta-doped TiO_2 dielectric deposited with ALD was reported to exhibit a leakage current density of 10^{-3} A/cm^2 at 1 MV/cm.⁹ Co-ALD of ZrO_2 and TiO_2 , $\text{Zr}_x\text{Ti}_{1-x}\text{O}_2$, was found to result in films with a dielectric constant of ~ 20 and a leakage current of 10^{-5} A/cm^2 at 1 MV/cm, while its preferred amorphous state was maintained up to 600°C .⁵ Thus, the electrical properties of optimized amorphous $\text{Er}_{1-x}\text{Ti}_x\text{O}_y$ films in our study include a dielectric constant of ~ 36 , hysteresis voltages of less than 10 mV, trapped charge densities of $\sim 10^{11} \text{ cm}^{-2}$, flatband voltages of $\sim -0.3 \text{ V}$, and leakage current densities of 10^{-8} A/cm^2 at -1 MV/cm on Si.

Conclusions

A combination of binary ALD processes was developed and demonstrated for the growth of $\text{Er}_{1-x}\text{Ti}_x\text{O}_y$ dielectrics using tris(methylcyclopentadienyl)erbium and tetrakis(diethylamino)-titanium as metal precursors with O_3 as oxidant. The growth rates of Er_2O_3 and TiO_2 with temperature-optimized ALD conditions were found to be 0.12 and 0.047 nm/cycle, respectively. A sufficient overlapping temperature window of $(\text{CpMe})_3\text{Er}/\text{O}_3$ and TDEAT/ O_3 processes was obtained between 175 and 250°C . The atomic ratio of $\text{Er}/(\text{Er}+\text{Ti})$ in $\text{Er}_{1-x}\text{Ti}_x\text{O}_y$ films was found to increase monotonically with increasing normalized cycle ratio of $\text{Er}_2\text{O}_3/(\text{Er}_2\text{O}_3 + \text{TiO}_2)$, showing excellent tunability of the thin film composition. No nitrogen and carbon contamination was detected in the film. Interfacial layer XPS studies suggested the presence of silicate and silicon oxide after deposition, while an increased formation of SiO_2 was observed after RTP at 700°C in O_2 at 1 atm. TiO_2 was found to start crystallizing at the ALD conditions used as detected by GIXRD and the as-deposited TiO_2 showed a relatively small rms roughness value; after RTP, a sharp increase in the intensity of the crystalline features along with a larger rms value corroborated a mostly amorphous-to-anatase phase transition. $\text{Er}_{1-x}\text{Ti}_x\text{O}_y$ films deposited with ALDCR of 1:8 or higher showed desired levels of uniformity, surface roughness, and good thermal stability up to 700°C . The resulting amorphous $\text{Er}_{1-x}\text{Ti}_x\text{O}_y$ films after RTP treatment showed a dielectric constant of ~ 36 , small hystereses (i.e., less than 10 mV), low trapped charge densities ($\sim 10^{11} \text{ cm}^{-2}$), and low leakage current densities on the order of 10^{-8} A/cm^2 at -1 MV/cm on p-type Si. Therefore, the incorporation of Er into TiO_2 combined with the RTP treatments used exhibited a remarkable improvement over pure TiO_2 films ($J = 10^{-2} \text{ A/cm}^2$ at -1 MV/cm).

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