Fabrication and Electrical characteristic of quaternary ultrathin HfTiErO thin films for MOS devices grown by rf sputtering

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Abstract

Ultra-thin Ti and Er co-doped HfO_2 films were grown on Si substrate by RF sputtering at different compositions and subjected to rapid thermal annealing at 500 °C and 700 °C in nitrogen ambient for 60 s. Dielectric properties of ultrathin co doped with Tritium and Erbium into hafnium oxide (HfO_2) with rapid thermal annealing (RTA) have been investigated. Ti and Er different contents doped HfO_2 thin films about (5 to 10) nm thicknesses have been employed for Au/HfTiErO/Si/Au metal oxide semiconductor (MOS) structures fabrication. The fabricated MOS (Au/HfTiErO/Si/Au) structure has been used for extracting electrical properties such that, dielectric constant, effective charge carriers, flat band voltage, interface trap density and doping concentration through capacitance voltage measurements. The films compared at different contents used for Ti and Er doped with HfO_2 on growth parameters, which could not showed excellent properties due to small thickness and other several defects during the depositions. While, the film annealed at 500 °C has the improved microstructure and electrical characteristics. Furthermore Atomic force microscopy and X-ray photo electron microscopy analysis verified the microstructure of HfTiErO gate oxide for future MOS devices.

Keywords: high-k, HfTiErO, Thin films, rf Sputtering

1. Introduction

In order to resolve the problem of device compatibility, reliability and high gate leakage currents, Recently, high-k gate dielectrics are explored to replace conventional SiO_2 as an alternative gate dielectric materials(Schaller *et al*., 2004). There are several high-k dielectric material have been introduced to replace it one the suitable material is HfO_2, which has been considered a suitable high-k gate dielectrics material for integration in complementary metal oxide semiconductor (CMOS) devices because of its good thermal stability and wide band gap on Si (Wilk *et al*., 2001). Unfortunately, besides the merits, there are several drawbacks of HfO_2 ZrO_2, Al_2O_3 and Y_2O_3 (Akbar *et al*., 2003) (Mikhelashvili *et al*., 2001) (Buchanan *et al*., 1999) dielectric materials. All these materials have a very low crystallization onset temperature on silicon, which caused the formation of interfacial layers often occurs. However, it was also observed that the mobility reduces when the Vfb of hafnium oxide shifts with the increasing of EOT. The degradation of Vfb and poor mobility are the results of crystallization, which produces the oxygen vacancies in the interfacial layer and in the high k layers when these materials are deposited on Si. The existence of any interfacial layer of silicate material or silicon dioxide will limit the highest possible gate stack capacitance and produce a variation of electrical properties(Yamamoto *et al.*, 2006). Moreover, the occurrence interfacial layer on dielectric/Si which degrade the device performance. To attain new aggressive scaling, recently hafnium based dielectrics materials have been proposed for the next generations (Chen *et al*., 2004) (Auciello, *et al* 2005). it has been reported that doping of Er, Dy, Nd, or Tb or TiO_x into hafnium oxide dielectric films showed excellent electrical characteristics (Först et al., 2005) (Klie *et al*., 2003) and the physical properties were investigated by using x-ray photoelectron spectroscopy (XPS) (Kim *et al*., 2004). However, the electrical, dielectric, microstructure and optical, properties of ultrathin films depend strongly on the growth conditions fabrication process, and post deposition annealing treatment.

A number of methods and deposition techniques have been employed to attain fine quality of high-k thin films, for instance chemical vapor deposition (CVD), molecular beam-epitaxy (MBE) atomic layer deposition (ALD) , reactive thermal evaporation and pulsed-laser deposition (PLD) etc (Dey *et al*., 2004) (Park *et al*., 2002) (He *et al*., 2007)

(Ergin *et al.*, 2010). Although RF sputtering (Ergin *et al*., 2010) is PVD based technique combined with plasma offers a low temperature processing and blocks the oxygen from the ambience, which prevents the formation of interfacial layer (IL). Therefore, in this work RF sputtering technique explores the possibility of obtaining the good quality high-k gate dielectric thin films, which is the most important requirement of advanced CMOS technology.

In the present study, HfO_2-based thin layers have been fabricated by RF magnetron sputtering of a pure HfO_2 with Ti and different Er targets in pure argon plasma. The fabrication and electrical properties of the ultrathin films have been analyzed by means of such as atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS) and capacitance-voltage (C-V) with respect to the deposition conditions and the annealing treatments. A special focus of the study is to reveal the relationship between Er-doped content and the surface roughness, chemical compositions and electrical properties.

2. Experimental

Before deposition, N-type Si (1 0 0) wafers with a resistivity of (1-10) Ω- cm were cleaned by a modified RCA process, (using ultrasonic bath into different chemicals such as, acetone, alcohol and di-ionized water for 5 minutes each. To remove any native oxide and hydrogen passivity on the surface, substrate was dipped in 1% buffered Hf solution. Cleaned substrates were dried by N_2 and put into the deposition chamber of JGP450 vacuum magnetron sputtering equipment. The deposition was performed under a mixture of Argon (Ar) and oxygen (O_2) ambient supplied as reactive gases, respectively. Hafnium disk of 99.99% purity with the diameter of 60 mm was used as the sputtering main target, while other targets titanium and erbium were fixed on the main target disk. The sputtering chamber was evacuated with lowest pressure about 3×10^{-4} Pa before Ar and O_2 gases were used. The target was pre-sputtered in argon (Ar) ambient for 10 min in order to remove surface oxide on the target, prior to HfTiErO deposition. During the deposition process, the RF power, substrate temperature, working pressure, substrate-to-target distance, total gas-flow rate were kept at 100 W, 250 ℃, 0.7 Pa, 5.5 cm, and 0.4 ratio, respectively. In order to obtain HfTiErO films with different Ti and Er contents. There is different Ti and Er materials were introduced on Hafnium oxides, after deposition the ultra thin films were annealed in N2 atmosphere for 60 s at 500 °C and 700 °C temperatures.

2.1 C-V Characterizations

Electrical properties of the MOS capacitor were measured using a using HP 4294A LCR meter, impedance/gain-phase analyzer. CET was extracted from an accumulation capacitance measured at 1MHz, without deducting for the quantum mechanical effect. The voltage of the external signal is 30mV and the external DC bias scanning with the order of -4V—> +4V—> -4V.

2.2 AFM and XPS characterization

The microstructure and chemical composition of the deposited material were characterized by using AFM and XPS. In the work the primitive CSPM5000 series of scanning probe microscopy used to analysis the sample's film surface morphology, while Chemical composition of the elements were made at The Experimental Analysis Center, Tsinghua University by X-ray photoelectron spectroscopy (XPS) using PHI Quantera SXM with 45 °take-off angle.

3. Result and discussions

3.1 Atomic force microscopy (AFM)

The AFM research on the surface roughness to check the surface morphology of both as-deposited and annealed films, especially high-k materials, appears very significant because this is an important physical property that may affect the electrical properties of dielectric thin films and induces shifts in electronic energy levels (Song *et al.*, 2007) and (Tao *et al.*, 2011). To expose the relationship between the doping content of Er and surface morphology the AFM images were taken for all samples as deposited and in N_2 ambient at 500 ℃ and 700 ℃ for 60 s and are shown in Fig. 1. The samples were scanned at the size of 2 × 2 μm. It can be observed from the results that the surface roughness of films is improved slightly by increasing the Er concentration. The results demonstrated that the films display a homogeneous and smooth surface structure, by means of a homogeneous material distribution with a low surface roughness after the provide annealing temperatures at 500 ℃ and 700 ℃. The AFM analysis of both as deposited and annealed films show the root mean square (RMS) surface roughness calculated from the AFM images for S1, S2, S3, S4 and S5 are approximately 5.0nm, 4.0nm, 3.8nm, 3.0nm and 3.2nm, respectively. It is remarkable to find that the surface of S1 and S2 samples consist of dense narrow spikes in shape, whereas the samples S4 and S5 are more mountain like, flat and void free. This spiky augment in roughness for S2 and S3 is possibly attributed to a transformation of phase structure. It was also reported that the amorphous structure of the thin film is changed into the polycrystalline structure after annealing; due to the increase of the grain size will result in an increase of the surface roughness (Cho *et al*., 2006). This may shows that the surface of films acquires smoother after annealing process. The diffusion and mobility of the surface atoms can be increased by increasing the annealing temperature, which provides energy to surface atoms. Due to transfer of such atoms to existing voids and defects, the surface gets smoother and reduces the surface roughness

3.2 XPS

The Chemical compositions of the elements were made by using X-ray photoelectron spectroscopy (XPS) using PHI Quantera SXM with 45° take-off angle. The XPS profiles for the samples (1), (2), (3), (4) and (5) (S1-HfTi6O, S2-HfTi6Er2O, S3-HfTi6Er4O, S4-HfTi6Er4O at 500℃ and S5-HfTi6Er4O at 700℃) are shown in Fig.2. It can be seen that a series of peaks from Hf4f, Er4d, Hf4d, C1s, Ti2p and O1s arisen from the surface contamination of adventitious carbon are clearly observed. Annealing leads to the removal of C1s peaks for the samples (2) and (4). Effects of experimental charging were corrected by setting the C1s peak for adventitious carbon at 284.6 eV. The different percentage ratios of the content were analysis and are shown in table.1.

3.3 MOS fabrications and C-V measurements:

The MOS structure of the gate dielectric is helpful to understand the various electrical characteristics of the high-k dielectric materials, such as the relative permittivity of the high-k dielectric, there are various charge defects inside the thin film and the Si substrate contact interface characteristics and so on. However, to investigate the impact of Ti and Er addition in HfO_2 films, capacitors with MOS electrodes were fabricated. Fig.3 showed well-behaved capacitance-voltage (C-V) curves for the target of HfTiErO films at different Er contents. All HfTiErO films, regardless of their Er content, have a nominal flat band voltage (Vfb) shift relative to the HfTiO while sample HfTi6Er4O shows the highest capacitance density relative to the rest of the other samples. Whereas from the C-V cures it can be seen that the geometry of all as deposited sample curves is not symmetric possibly due to the ultra thin thickness which might be caused of leakage current. The detailed analysis of the different value of Er doped HfTiO films at different Er contents. Results indicate that of all the different Er contents, HfTiO is the not most promising on substrate temperatures. The films have the highest leakage of current.

3.4 Annealed C-V curves.

Fig.4 demonstrates high frequency C-V characteristics of annealed HfTiErO gate dielectric MOS capacitors. According to the accumulation capacitance, it can be seen that the film annealed at 500 °C has improved electrical properties as compare to without annealed samples.

It can be seen that films annealed temperature at 500 °C has the improved Electrical properties, almost samples have very high k dielectric constant may be resulted from the microstructure change such as crystalline. We also obtained the flat band voltage (Vfb) from C-V curves. Vfb primarily depends on deficiencies in HfTiErO film and the interface traps at the interface. The interfacial layer is formed unavoidably and after annealing the thickness of the film decreased, the reason lies in that with the increase of temperature, SiOx in gradually converted into silicate by the reaction of between HfTiErO and SiOx. The Ultrathin HfTiErO films annealed at 500 °C in nitrogen atmosphere temperature interfacial SiOx completely converted into silicate, which explained in many previous literatures (Ye *et al*., 2010).

According to the accumulative capacitance, the dielectric constant k can be calculated. It can be seen that at sample HfTi6Er4O has the highest k value of 30.0 as compare to other samples. This may be due to the SiOx completely converted into silicate, which demonstrated good interfacial quality (Ye *et al.*, 2011) . The permittivity value extracted from 1 MHz C-V curves are usually underestimated due to the well-known effect of series resistance on the capacitance at accumulation which is stronger at higher frequencies (Li *et al*., 2008). All sample having good electrical properties although the sample HfTi6Er4O films achieved best electrical properties as compare other samples.

5. Conclusion

In summary, a higher-k material HfTiErO has been demonstrated. Its amorphous structure is sustained up to a post annealing temperature of 500 °C. By incorporating TiO_2 and Er_2O_3, the dielectric constant could be increased with other electrical properties. Moreover, XPS Hf 4f and O1 s results can be concluded that ultra thin HfTiErO films microstructure is formed, while the anealed temperature also effected on the the microsturuture that caused the increase in intensity and binding energy as well. These improved material and electrical results indicate that HfTiErO may be a promising candidate for the next generation of higher-k gate dielectrics.

References

Schaller RR. Technological innovation in the semiconductor industry: A case study of the international technology roadmap for semiconductors (ITRS). thesis. George Mason University, 2004

Wilk GD, Wallace RM, Anthony JM. High-κ gate dielectrics: Current status and materials properties considerations. Journal of Applied Physics, 2001, 89: 5243

Akbar MS, Gopalan S, Cho H-J, *et al*. High-performance TaN/HfSiON/Si metal-oxide-semiconductor structures prepared by NH3 post-deposition anneal. Applied Physics Letters, 2003, 82: 1757-1759

Mikhelashvili V, Eisenstein G, Edelmann F. Characteristics of electron-beam-gun-evaporated Er_2O_3 thin films as gate dielectrics for silicon. Journal of Applied Physics, 2001, 90: 5447

Buchanan D. Scaling the gate dielectric: Materials, integration, and reliability. IBM journal of research and development, 1999, 43: 245-264

Yamamoto Y, Kita K, Kyuno K, et al. Structural and electrical properties of HfLaOx films for an amorphous high-k gate insulator. Applied Physics Letters, 2006, 89: 032903

Chen F, Bin X, Hella C, *et al*. A study of mixtures of HfO_2 and TiO_2 as high-k gate dielectrics. Microelectronic Engineering, 2004, 72: 263-266

Auciello O, Fan W, Kabius B, *et al.* Hybrid titanium–aluminum oxide layer as alternative high-k gate dielectric for the next generation of complementary metal–oxide–semiconductor devices. Applied Physics Letters, 2005, 86: 042904-042904-042903

Först CJ, Schwarz K, Blöchl PE. Structural and electronic properties of the interface between the high-k oxide $LaAlO_3$ and si (001). Physical review letters, 2005, 95: 137602

Klie R, Browning N, Chowdhuri AR, *et al.* Analysis of ultrathin SiO interface layers in chemical vapor deposition of AlO on Si by in situ scanning transmission electron microscopy. Applied Physics Letters, 2003, 83: 1187

Kim J, Yong K. Characterization of hafnium silicate thin films grown by MOCVD using a new combination of precursors. Journal of Crystal Growth, 2004, 263: 442-446

Dey S, Das A, Tsai M, *et al*. Relationships among equivalent oxide thickness, nanochemistry, and nanostructure in atomic layer chemical-vapor-deposited Hf–O films on Si. Journal of Applied Physics, 2004, 95: 5042-5048

Park BK, Park J, Cho M, *et al*. Interfacial reaction between chemically vapor-deposited hfo thin films and a Hf-cleaned Si substrate during film growth and postannealing. Applied Physics Letters, 2002, 80: 2368

He G, Zhu L, Liu M, *et al.* Optical and electrical properties of plasma-oxidation derived HfO_2 gate dielectric films. Applied Surface Science, 2007, 253: 3413-3418

Ergin FB, Turan R, Shishiyanu ST, *et al.* Effect of γ-radiation on HfO_2 based MOS capacitor. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, 2010, 268: 1482-1485

Song X, Takoudis CG. Cyclic chemical-vapor-deposited TiO_2/Al_2O_3 film using trimethyl aluminum, tetrakis (diethylamino) titanium, and O_2. Journal of The Electrochemical Society, 2007, 154: G177-G182

Tao Q, Kueltzo A, Singh M, *et al.* Atomic layer deposition of HfO_2, TiO_2, and $Hf_xTi_{1-x}O_2$ using metal (diethylamino) precursors and HfO_2. Journal of The Electrochemical Society, 2011, 158: G27-G33

Cho D-Y, Oh S-J, Chang Y, et al. Role of oxygen vacancy in $HfO_2/SiO_2/Si$ (100) interfaces. Applied Physics Letters, 2006, 88: 193502-193502-193503

Ye C, Wang H, Zhang J, *et al.* Composition dependence of band alignment and dielectric constant for $Hf_{1-x}Ti_xO_2$ thin films on si (100). Journal of Applied Physics, 2010, 107: 104103

Ye C, Wang Y, Zhang J, *et al.* Evidence of interface conversion and electrical characteristics improvement of ultra-thin HfTiO films upon rapid thermal annealing. Applied Physics Letters, 2011, 99: 182904-182904-182903

Li CX, Zou X, Lai PT, *et al.* Effects of Ti content and wet-N_2 anneal on Ge MOS capacitors with HfTiO gate dielectric. Microelectronics Reliability, 2008, 48: 526-530

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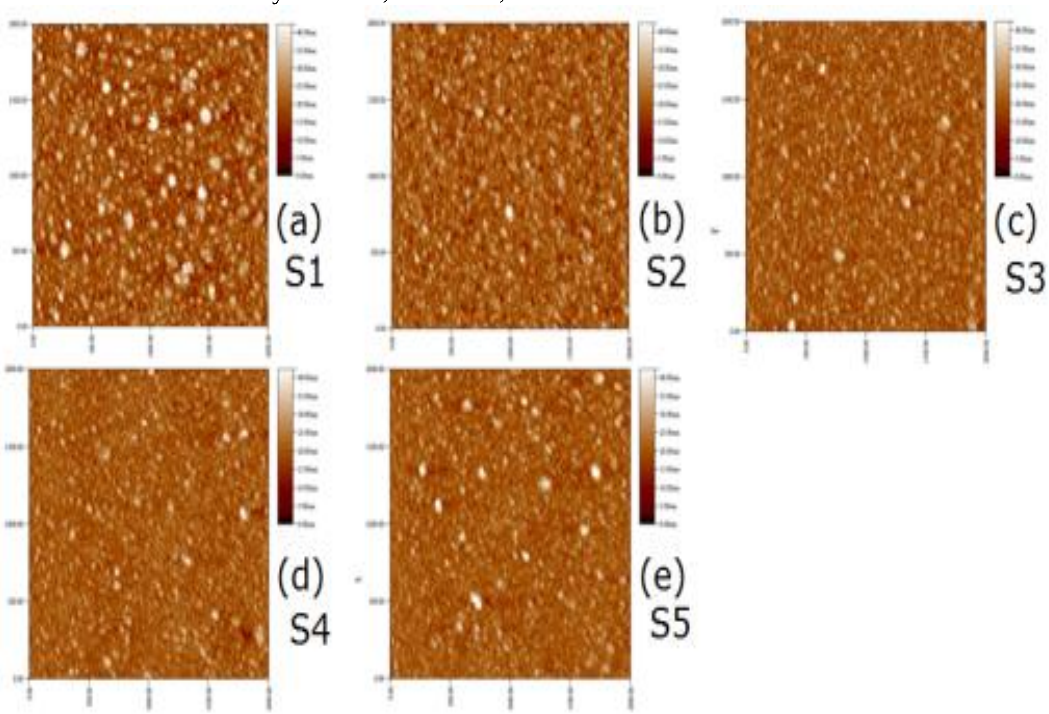

Figure 1. AFM surface images (2 × 2 μm) of different samples as deposited and annealed

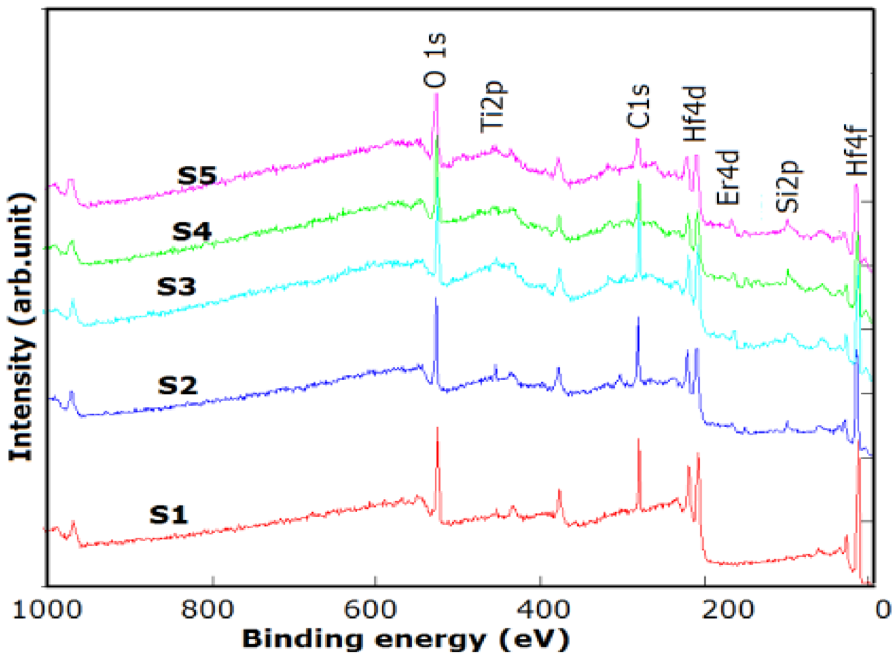

Figure 2. Typical XPS spectrum of as grown and annealed samples

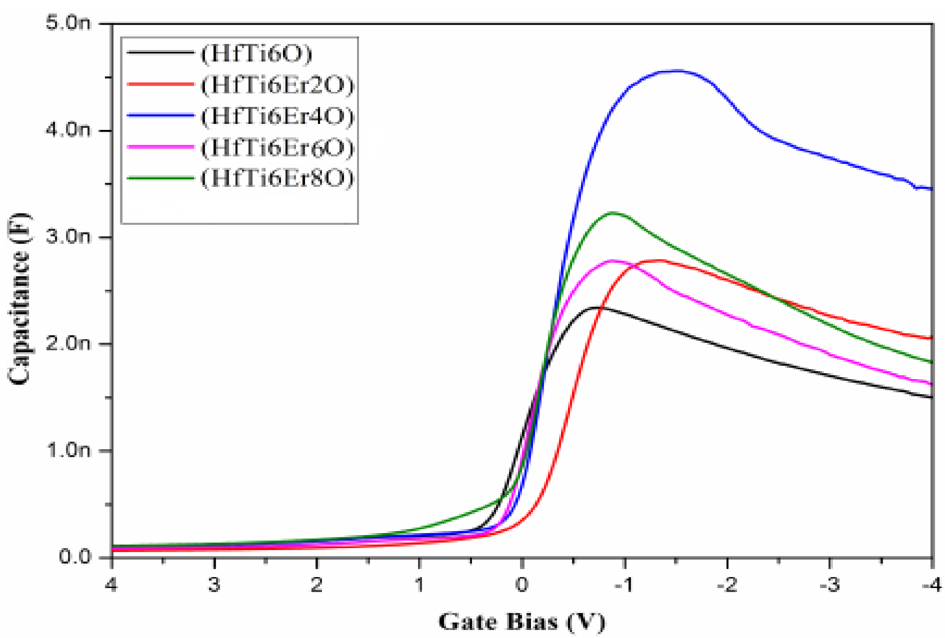

Figure 3. C-V curves of Er doped HfTiO films at different Er contents

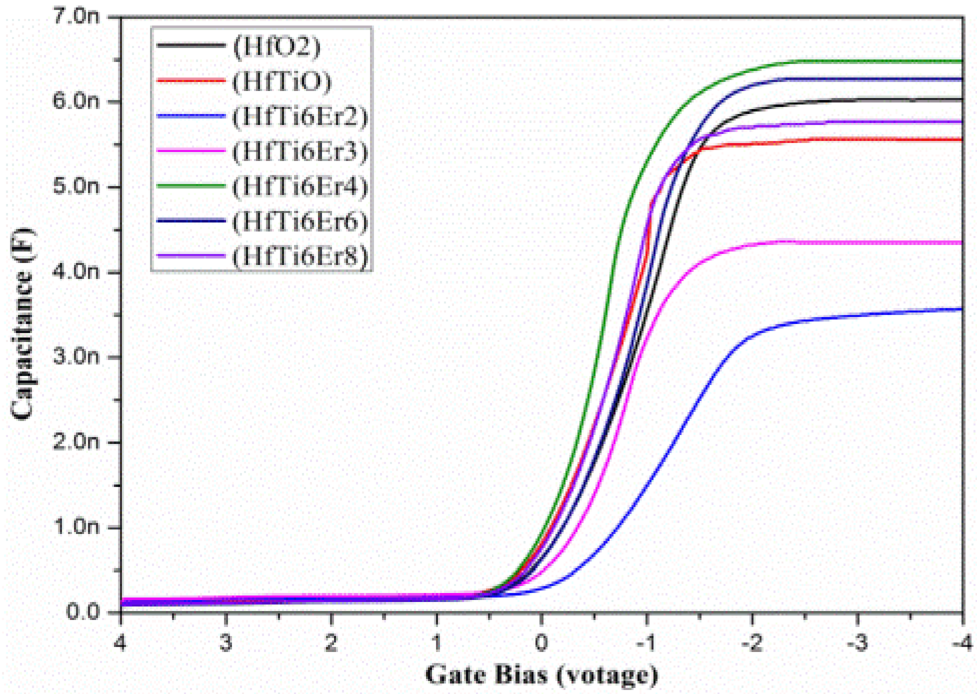

Figure 4. High frequency C-V curves for annealed HfTiErO thin films

Table 1. Atomic concentrations of different elements

	C1s	O1s	Si2p	Ti2p	Er4d	Hf4f
	[0.314]	[0.733]	[0.368]	[1.385]	[2.650]	[2.901]
S1	42.70	40.02	2.21	1.43	0.00	13.64
S2	43.94	37.53	8.10	1.36	0.84	8.24
S3	47.22	36.84	4.15	1.01	2.00	8.78
S4	36.58	43.08	10.80	1.02	1.38	7.14
S5	30.99	48.98	8.66	1.60	1.73	8.04