

# Defect reduction in non-crystalline and nano-crystalline thin films: chemical bonding self-organizations and minimization of macroscopic strain

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A study of changes in nano-scale morphology of thin films of nano-crystalline transition metal (TM) elemental oxides, HfO<sub>2</sub> and TiO<sub>2</sub>, on plasma-nitrided Ge(100) substrates, and Si(100) substrates with ultra-thin (~0.8 nm) plasma-nitrided Si suboxide, SiO<sub>x</sub>, x<2, or SiON interfacial layers is presented. Near edge X-ray absorption spectroscopy (NEXAS) has been used to determine nano-scale morphology of these films by Jahn-Teller distortion removal of band-edge d-state degeneracies. These results identify a new and novel application for NEXAS based on the resonant character of the respective O K<sub>1</sub> and N K<sub>1</sub> edge absorptions. This paper also includes a brief discussion the integration issues for introduction this Ge break-through into advanced semiconductor circuits and systems.

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## 1. Introduction

This paper provides the discovery of an intermediate phase in a non-crystalline Hf Si oxynitride ternary alloy that has important implications for the extension of Moore's Law scaling for complementary semiconductor metal oxide semiconductor (CMOS) scaling beyond the limits of Si technology by demonstrating how this dielectric can be integrated in Ge pMOS and nMOS devices. A significant problem in the development of field effect transistors on Ge substrates is the formation of *defective* interfacial transition regions with Ge-O bonds between Ge substrates and gate dielectrics [1]. One solution is to deposit a thin Si layer on the Ge, and then form a passivating/protective SiON interfacial layer; however this adds to the equivalent oxide thickness [2]. An alternative approach for eliminating interfacial Ge-O bonds is presented. A sacrificial interfacial GeN layer is formed on the Ge substrate, protecting the substrate surface from oxidation during film deposition. This layer is removed by a post deposition anneal in Ar at 800 °C leaving high-κ HfO<sub>2</sub> and TiO<sub>2</sub> thin film dielectrics in direct bonding-contact with the Ge substrate with no detectable nitride or oxide transition region. This new and novel application for NEXAS relies critically on the resonant character of the X-ray absorption.

A second and equally import part of the paper addresses differences in defects in optimized nano- and non-crystalline Hf-based dielectrics, highlighting gate stack interface issues. This includes the interface with a Ge substrate, as well as the integration of either dual metal gates, or a single mid-gap gate dielectric.

## 2. Experimental methods and results

Nano-crystalline HfO<sub>2</sub> and TiO<sub>2</sub> films ~2 to 6 nm thick were deposited at 300 °C by remote plasma-enhanced chemical-vapor-deposition onto remote plasma-nitrided Ge substrates, and compared with HfO<sub>2</sub> and TiO<sub>2</sub> films deposited onto Si substrates with ~0.6-0.8 nm thick SiON interfacial layers. [1,2]. The combination of resonant atom-specific O K<sub>1</sub> and N K<sub>1</sub> absorptions is an effective way to study buried interfaces, and in particular relationships between bonding in oxide dielectrics, and interfacial transition regions.

Fig. 1 (a) shows the N K<sub>1</sub> spectrum for remote plasma assisted nitridation of Ge (100) substrates used for deposition of HfO<sub>2</sub> and TiO<sub>2</sub> films. Based on on-line Auger electron spectroscopy performed prior to film deposition, the GeN thickness is 0.8±0.1 nm. Films of HfO<sub>2</sub> and TiO<sub>2</sub> ~2 to 6 nm thick were deposited onto these nitrided Ge(100) substrates at 300°C, and then subjected to an ex-situ one minute 800°C rapid thermal anneal in Ar. Fig. 1(b) shows N K<sub>1</sub> spectra for buried interfaces for 2 nm and 6 nm thick HfO<sub>2</sub> films annealed at 800°C. These spectra indicate significantly reduced interfacial Ge-N bonding after the 800 °C anneal. The reductions are essentially the same even though the 6 nm film is three times thicker as the 2 nm film. Fig. 2 shows O K<sub>1</sub> spectra for HfO<sub>2</sub> (a) 2 nm thick, and (b) 6 nm thick on Ge(100) substrates, providing comparisons between films as-deposited at 300°C, and after the 800°C anneal in Ar. The O K<sub>1</sub> spectrum for the as-deposited 2 nm HfO<sub>2</sub> film in 2(a)

on the GeN interface shows broad spectral features that are different for the 800°C annealed 2 nm film which the GeN layers has been removed. The spectrum for the annealed film shows a band edge resolved doublet, and three other relative sharp features. There are similar qualitative differences for O K<sub>1</sub> spectra for 6 nm films, as-deposited, and after annealing at 800 °C, and these are displayed in Fig. 2(b).

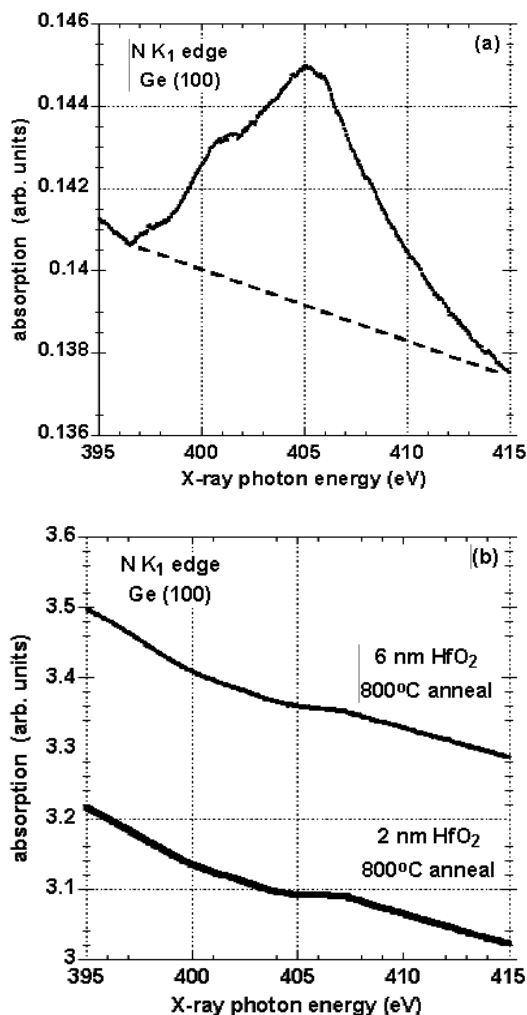


Fig. 1. N K<sub>1</sub> spectra for plasma assisted nitridation of Ge (100) substrates; (a) Ge substrate nitridation for all Ge samples; (b) buried interfaces for 2 nm and 6 nm thick HfO<sub>2</sub> films after 800 °C anneal.

The features in the O K<sub>1</sub> spectra in Fig. 2 are O 2p  $\pi$ , 532-535 eV, and O 2p  $\sigma$ , 536-539 eV, 542 eV and 544 eV molecular orbital (MO) states localized on the O-atoms; these MO states are mixed with atomic states of the Hf atoms in symmetry adapted MO final states [4]. The lowest energy Hf features for these nano-crystalline HfO<sub>2</sub> films between 532 and 535 eV have contributions from Hf E<sub>g</sub> anti-bonding  $\pi\pi$ -states, and the peak between 536 and 539 eV from Hf T<sub>2g</sub> anti-bonding  $\sigma$ -states, and features at ~542 and 544 eV have contributions Hf 6s A<sub>1g</sub> states, and

Hf 6p T<sub>1u</sub> states [3,4]. The scale of nano-crystallinity, i.e., grain size, is established by the relative intensities of the features in these O K<sub>1</sub> spectra [3,5].

The broader spectral features in the as-deposited films in Figs. 2(a) and 2(b) are attributed to a less than 2 nm nano-crystallites grain size, whilst the sharper features in 800°C annealed films are attributed to nano-crystallite grains > 3.5 to 4 nm [3,5]. This aspect of nano-crystallinity is based on the splitting of the band edge E<sub>g</sub> state into a doublet, and is attributed to a collective Jahn-Teller distortion, which removes the degeneracy. This requires a nano-scale grain size > 3.5 nm [3,5]. This length scale has been established by systematic studies of HfO<sub>2</sub> and ZrO<sub>2</sub> films on SiON interfaces using Si(100) substrates [3]. Additionally, the as deposited film 2 nm and 6 nm films display qualitative differences in the E<sub>g</sub> feature. These are attributed to changes in unit cell morphology as a function of film thickness, and are similar to results for 6 nm thick phase separated Hf silicates in Ref. 3.

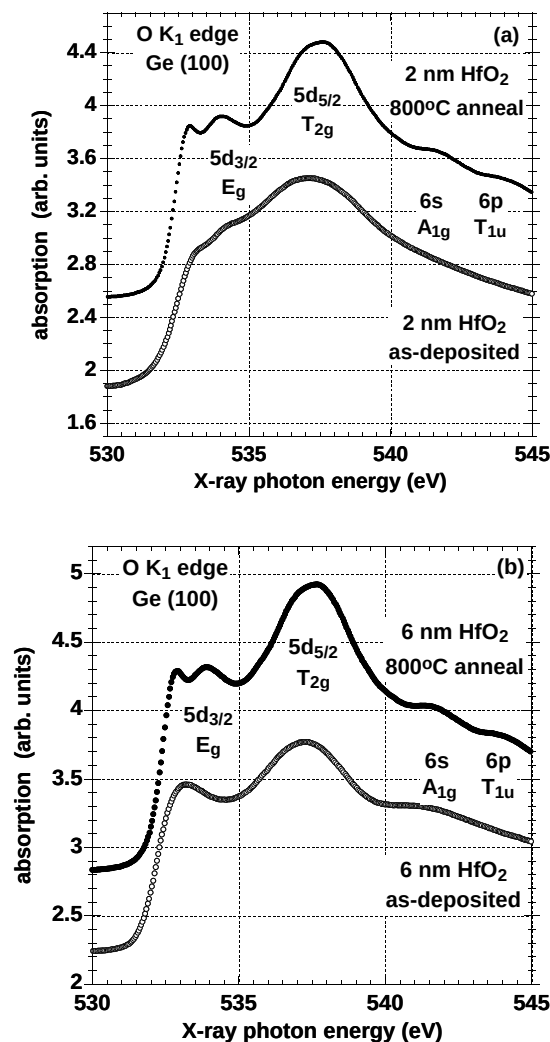


Fig. 2. O K<sub>1</sub> spectra for HfO<sub>2</sub> on Ge(100) substrates: comparisons between as-deposited at 300 °C, and after an 800 °C 1 minute anneal in Ar: (a) 2 nm thick, and (b) 6 nm thick.

Fig. 3(a) is for an as deposited and 900 °C annealed 2 nm thick film HfO<sub>2</sub> on an SiON interface on a Si substrate. The O K<sub>1</sub> spectrum displays broad features similar to those for the as-deposited 2 nm thick HfO<sub>2</sub> films in Fig. 2(a) [3]. The absence of J-T degeneracy splitting for the band-edge Hf E<sub>g</sub> features in these films is attributed a suppression of *coherent*  $\pi$ -bonding [3,5]. This *incoherent*  $\pi$ -bonding in 2 nm thick HfO<sub>2</sub> as-deposited and annealed films on SiON is consistent with homogenous nucleation of  $\sim$ 2 nm nano-grains with a length scale below the threshold level for *coherent*  $\pi$ -bonding [3]. The incoherent  $\pi$ -bonding after the 900 °C anneal is due to a dimensional constraint associated with the 2 nm film thickness. In marked contrast, *coherent*  $\pi$ -bonding with a J-T distortion is observed in annealed 6 nm thick film on SiON in Fig. 3(b) nano-grains are  $>$  3.5 nm; this nano-grain size is not constrained by the 6 nm film thickness [3]. In both of the as-deposited films, the incoherent  $\pi$ -bonding is a kinetic limitation associated with the low growth temperature. Finally, based on these comparisons, the J-T splittings in the Fig. 2(b) for annealed nm thick film on Ge is also indicative of a nano-grain size  $>$  3.5 nm, but in this case, it is not limited by film thickness.

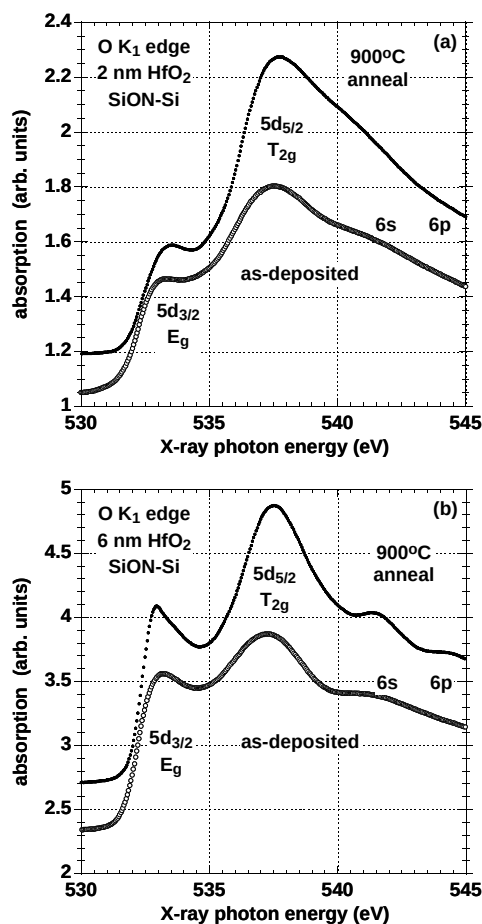


Fig. 3. O K<sub>1</sub> spectra for HfO<sub>2</sub> on Si(100) with SiON substrates as-deposited at 300 °C, and after a 900 °C 1 minute anneal in Ar (a) 2 nm, and (b) 6 nm.

The results for TiO<sub>2</sub> deposition onto nitrated Ge substrates parallel the results in Figs. 1 and 2 for HfO<sub>2</sub> on Ge substrates.

### 3. Discussion: Integration issues

#### 3.1. Dielectrics

Asymmetric trapping in discrete band edge electron and hole traps, inherent nano-crystalline HfO<sub>2</sub> thin film dielectrics  $>$  4 nm thick represent a significant limitation in the introduction of these films into CMOS devices [6-9]. Defect densities can be reduced by factors between 10 and 50 by constraining nano-grain thickness to  $\sim$  2 nm or less; however, band-tail, rather than discrete defects, are still present at both band edges, and it remains to be demonstrated that asymmetries in trapping are reduced to levels that permit CMOS operation [9,10]. This paper identifies a narrow composition range for pseudo-ternary Hf Si oxynitride alloys that are stable against CPS to temperatures  $>$ 1000 °C, have dielectric constants  $\sim$ 10 to 12, tunneling leakage  $<10^{-7}$  A-cm<sup>-2</sup> 1 V above  $V_{fb}$ , and defect levels and reliability comparable to SiO<sub>2</sub> [6]. This paper demonstrates that these electrical properties derive from strain reducing *chemically self-organized* bonding arrangements with length scale of  $\sim$ 0.8 nm, with a *percolation* of these strain reducing bonding Fig. 4(a) presents O K<sub>1</sub> spectra for thin films of HfO<sub>2</sub> deposited onto SiON interfaces ( $\sim$ 1 nm thick) with different physical thickness, and annealed at 700 °C. The spectra of the 2 nm and 4 nm thick films significant differences: i) the E<sub>g</sub> or Hf 5d<sub>3/2</sub> feature in the 4 nm film is a spectroscopically resolved doublet,  $\Delta E_{Eg} \sim$  1.2 eV, whereas in the 2 nm film it is a *single* feature; and ii) T<sub>2g</sub> (Hf 5d<sub>5/2</sub>), A<sub>1g</sub> (Hf 6s) and T<sub>1u</sub> (Hf 6p) features are sharper, and more easily resolved in the 4 nm film, compared with the 2 nm film. Spectral features in the 3 nm film are intermediate, but clearly display an asymmetric line-shape in the E<sub>g</sub> d-state feature due to degeneracy removal. This description of anti-bonding Hf states is based on symmetry adopted linear combinations (SALC) contributions Hf and O atomic states to the final molecular orbital states [13].

The spectral differences in Fig. 4(a) are interpreted by a physical thickness or *dimensionally controlled* limitation on  $\lambda_{coh}$ , the length scale for coherent bonding [10]. This results in either the direct observation of J-T degeneracy removal, or in a softening of the threshold edge slope. Spectral differences in Fig. 4(a) are consistent with  $\lambda_{coh} \approx$  3 nm; inter-PUC  $\pi$ -bonding interactions are suppressed in the 2 nm film, but coherent  $\pi$ -bonding interactions with J-T splittings are evident in 3 and 4 nm thick films.

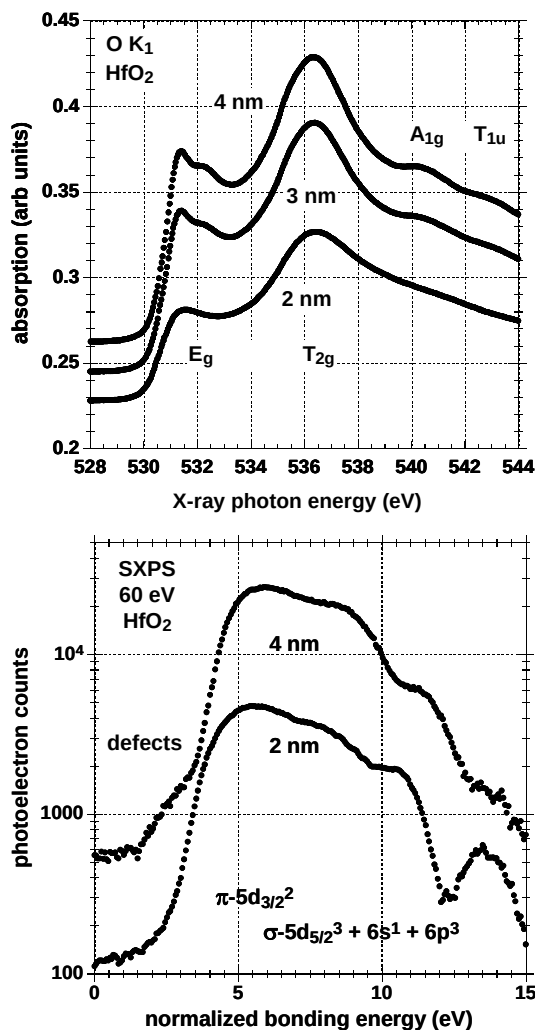


Fig. 4. Spectra for HfO<sub>2</sub> films annealed in Ar at 700 °C. (a) O K<sub>1</sub> edge spectra; films 2, 3 and 4 nm thick. (b) SXPS spectra films 2 nm and 4 nm thick showing differences in band edge defects.

Defect states in HfO<sub>2</sub> nano-crystalline films are qualitatively different in two different length scale regimes. For grain sizes > 3–4 nm, they are discrete band edge states associated with O-atom vacancies clustered at grain boundaries, whereas in as-deposited films, and films with a physical thickness of ~ 2 nm, they are band-tail defects with a density reduced by more than one order of magnitude. State differently, there is a direct correlation between the character of defects in nano-crystalline films that display J-T splittings in O K<sub>1</sub> edge spectra, and those that do not. Fig. 5(b) illustrates the qualitative and quantitative differences in valence band edge defects for HfO<sub>2</sub> thin films of different thickness. Behavior of defects at the respective conduction band edges are similar, with band edge discrete defects in films > 4 nm thick, being replaced by reduced densities of band-tail defects at both band edges.

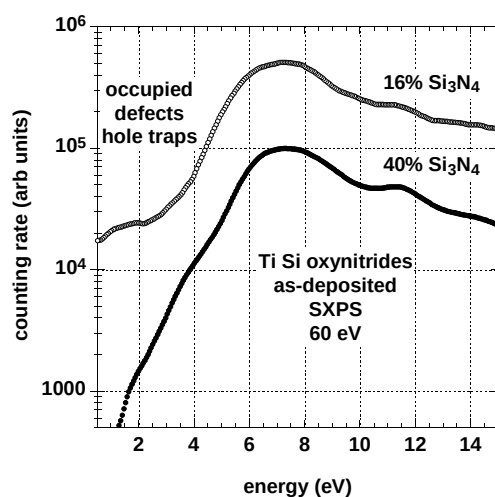


Fig. 5. SXPS valence band spectra Ti Si oxynitrides comparing defects for 16 and 40% Si<sub>3</sub>N<sub>4</sub> alloys.

Figs. 6(a) and 6(b) show leakage current versus applied voltage for Si substrate injection of electrons in MOSCAPS with as-deposited Hf Si oxynitride dielectrics fabricated on n-type Si substrates with Al gate electrodes ( $V_{fb} \sim 0.0$  V). Fig. 6(b) displays leakage current for  $V_g - V_{fb} = 1$  V, versus Si<sub>3</sub>N<sub>4</sub> content for ~equal SiO<sub>2</sub> and HfO<sub>2</sub> content. There is a significant reduction in leakage for a narrow range of compositions at ~40% Si<sub>3</sub>N<sub>4</sub>.

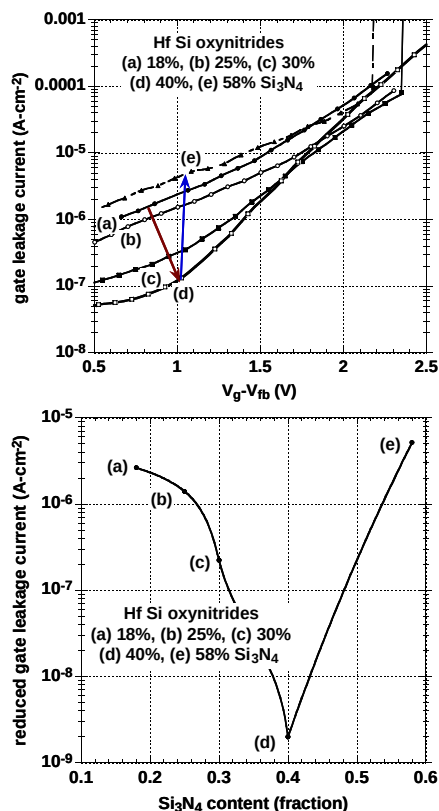


Fig. 6. (a) Gate leakage current versus  $V_g - V_{fb}$ . (b) Normalized gate leakage current versus Si<sub>3</sub>N<sub>4</sub> content.

Figs. 7(a) and 7(b) compare C-V traces for 18% and 40%  $\text{Si}_3\text{N}_4$  with  $\sim$ equal  $\text{SiO}_2$  and  $\text{HfO}_2$  content. The  $V_{fb}$  voltage indicated a fixed interfacial charge  $<10^{11} \text{ cm}^{-2}$  for the 40% alloy, and a positive fixed charge  $\sim 0.5 \times 10^{12} \text{ cm}^{-2}$  for the 18% alloy. The frequency dispersion of the C-V characteristics is different between 1 MHz and 100 kHz indicating a  $D_{it}$  level  $\sim 10^{12} \text{ cm}^{-2}$  for substrate hole injection or the 18% alloy, and  $>10\times$  lower for the 40% alloy.

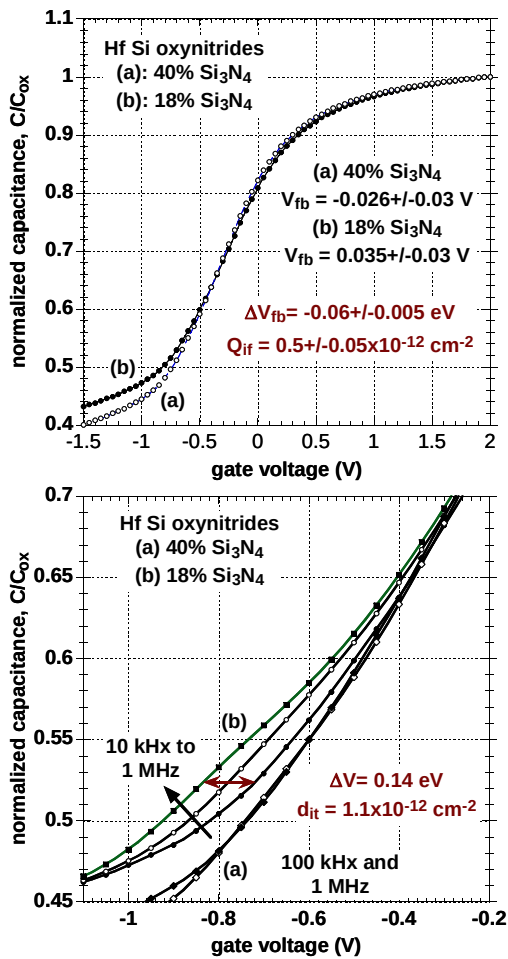


Fig. 7. (a) Capacitance versus gate voltage. (b) Limited voltage range capacitance versus gate voltage.

Total-dose X-ray irradiation response of low- and high- $\text{Si}_3\text{N}_4$  content Hf Si oxynitrides has been compared with  $\text{SiO}_2$  devices, and devices with Hf- based dielectrics [11]. The low level of hole trap generation in the high- $\text{Si}_3\text{N}_4$  content Hf Si oxynitride films was comparable to  $\text{SiO}_2$  devices confirming the validity of the predicted strain reduction. In contrast, there is significant electron trapping in  $\text{HfO}_2$  devices.

Low direct tunneling currents and reduced defect densities in the  $\sim 40\%$   $\text{Si}_3\text{N}_4$  content Hf, Zr, Ti and mixed [Hf,Ti] alloy Si oxynitrides, as well, are the result of self-organized chemical bonding arrangements that *minimize and effectively eliminate* macroscopic strain, thereby reducing defect levels [12]. These compositions are not

associated crystalline phase bonding, and occupy a very small fraction of the  $\text{HfO}_2$ ,  $\text{SiO}_2$  and  $\text{Si}_3\text{N}_4$  ternary phase diagram. Alloys along the join-line from  $\text{SiO}_2$  to  $\text{Si}_3\text{N}_4$ , are stable with respect to CPS, and the 50-50 alloy has extended CMOS EOT scaling beyond the performance limitations of  $\text{SiO}_2$ . Hf silicates along the join-line from  $\text{SiO}_2$  to  $\text{HfO}_2$  are unstable against CPS; however,  $\text{HfO}_2$  rich alloys, e.g., 80%  $\text{HfO}_2$ -20%  $\text{SiO}_2$  are inverted silicates with  $\text{SiO}_2$  inclusions limiting nano-crystalline size, and thereby reducing defect levels with respect to  $\text{HfO}_2$  through elimination of grain boundaries [10]. With the exception of alloys with 35 to 45%  $\text{Si}_3\text{N}_4$ , and  $\sim$ equal  $\text{SiO}_2$  and  $\text{HfO}_2$ , all other ternary alloys are unstable against CPS, and have degraded electrical properties after annealing.

### 3.2. Ge CMOS devices

High performance pMOSFETs have been fabricated on oxidized/nitrided Ge/Ge substrates with high-k dielectrics:  $\text{HfO}_2$  and  $\text{ZrO}_2$  [14,15]. nMOSFETs are not adequate for CMOS, and these have been written off technology roadmaps; the a high density of defects at the Ge/passivating dielectric interface [15]. This has lead to proposals for a dual channel solution for future generations of scaled CMOS devices: GaAs/InGaAs substrates for nMOSFETs and Ge for pMOSFETs [16].

Near edge X-ray absorption (NEXAS) as SSRL, and vis-vacuum UV spectroscopic ellipsometry (vis-VUV SE) [5] are used to i) identify the alignment between the Ge substrate, a  $\text{GeO}_2$  interfacial transition region, and a  $\text{ZrO}_2/\text{HfO}_2$  high-k gate dielectric [8], and ii) determine this is compatible with formation of a channel through inversion of p-type Ge. Fig. 8 indicates NEXAS spectra for  $\text{SiO}_2$  and  $\text{GeO}_2$  interfacial layers/regions (IRs) on Si and Ge substrates. The  $\sim 2.5 \text{ eV}$  shift in energy between these edges is the  $\text{SiO}_2$  and  $\text{GeO}_2$  band gap difference. Since the valence band energies of  $\text{GeO}_2$  and  $\text{SiO}_2$  are  $\sim$ the same, the conduction band of  $\text{GeO}_2$  lines up close to that of Ge (and Si), obviating use of  $\text{GeO}_2$  as dielectric for nMOSFETs.

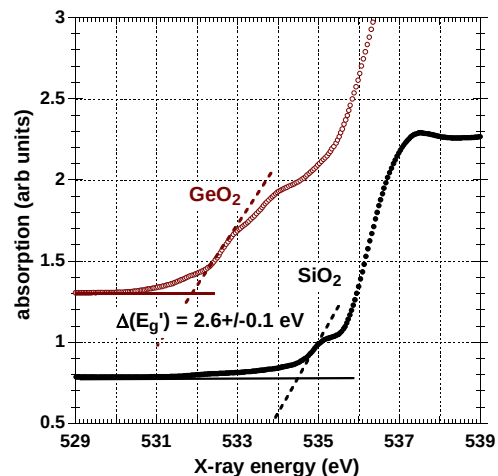


Fig. 8. O K<sub>1</sub> edge spectra for oxidized Ge and Si, indicating respectively, NEXAS spectra for  $\text{GeO}_2$  and  $\text{SiO}_2$ .

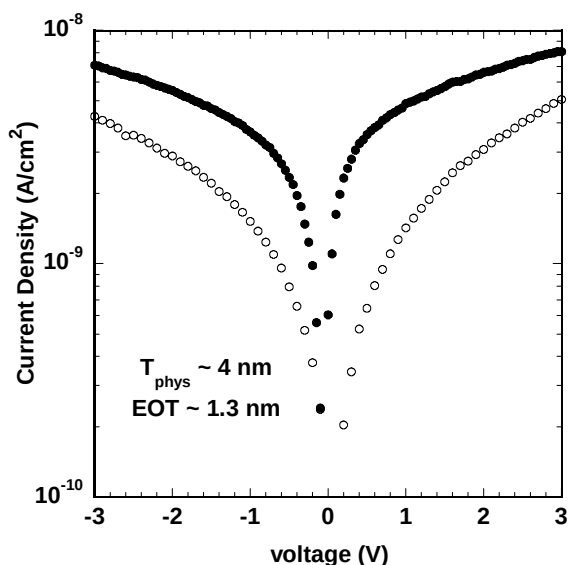


Fig. 9. Current voltage characteristics for n-Ge/Hf Si oxynitride (high  $\text{Si}_3\text{N}_4$  content)/Al for both substrate and gate injection of electrons. The physical thickness of the dielectric is  $\sim 4$  nm, and the effective oxide thickness (EOT) normalized to a dielectric constant of 3.8 for  $\text{SiO}_2$  is  $\sim 1.2$ -1.3 nm.

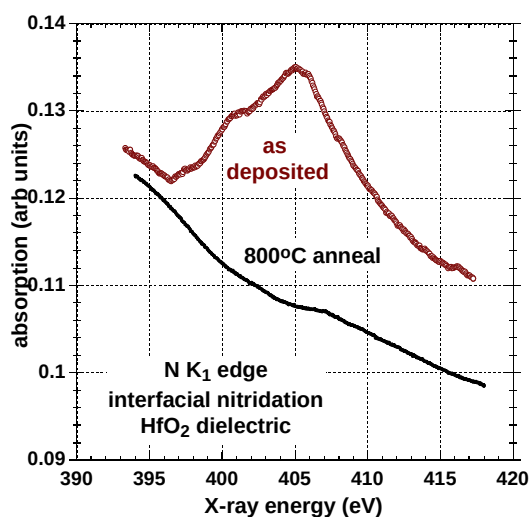


Fig. 10. Comparison of N  $K_1$  spectra for plasma assisted nitridation of Ge (100) substrates.

The obvious solution, demonstrated successfully in these results, is to eliminate a  $\text{GeO}_2$ , or oxide-contaminated GeN interface layer. This has been accomplished by plasma-processing as indicated in the I-V characteristics in Fig. 9 for MOSCAPs comprised of n-type Ge substrates, non-crystalline Hf Si oxynitride medium k dielectrics with low defect levels comparable to  $\text{SiO}_2$  [8], and Al metal gates (no heat treatment after deposition). This stacks line-ups with Fermi level in Al

with the Ge substrate. I-V curves for an EOT of 1.3 nm are very nearly symmetric indicating no interfacial transition region. The only difference between the two bias directions is due to a small voltage drop in the Ge substrate for gate injection. Absence of an IR has been verified by comparing N K and O K edge spectra for Hf Si oxynitride before and after removing the GeN used as a passivating layer during the dielectric deposition. This is a proof of concept for the development of Ge CMOS devices, a much more realizable pathway to scaling than using dual Ge-III-V substrates.

### 3.3. Metal Gates

One of the most significant and challenging process integration issues for high-k dielectrics has been the replacement of poly-Si gates for CMOS devices with either dual metal gates, or a single mid-band gap metal has been the stability of the metal gate/high-k gate dielectric interface to post deposition thermal processing. For elemental metals, the effective interfacial work function is approximated by the vacuum work function/electron affinity for as-deposited metals on high-k dielectrics such as  $\text{HfO}_2$ , but following post-deposition thermal annealing at modest temperatures, 500-700°C, the effective work function changes, and is typically driven to mid-gap.

There are two critical issues that are addressed in this work: i) can the interface between a metal gate electrode and a high-k oxide dielectric be atomically abrupt?, or,

ii) will there always be a chemically-graded interfacial transition region that mitigates the benefits of replacing dual poly-Si gates by metals?

Ab initio quantum mechanical calculations have been performed on cluster models of  $\text{Zr}(\text{Hf})/\text{Zr}(\text{Hf})\text{O}_2$  heterojunctions. These calculations indicate interfacial transition regions with suboxide bonding are formed by deposition of metal over-layers onto elemental oxides. These transition regions will be formed at metal high-k dielectric interfaces, either on deposition or after relatively low temperature (e.g., 700 °C) annealing, or processing. Therefore the integration issues for metal gates on dielectrics are essentially independent of the semiconductor substrate, e.g., Si or Ge, but depend of the gate electrode material and the dielectric. It is not obvious that the formation of metal gate transitions regions will be different on nano-crystalline and non-crystalline oxide dielectrics, but there may indeed be important technological differences for strongly nitrided dielectrics such as the Hf Si oxynitrides addressed above. Studies of the electrical performance of  $\text{HfO}_2$  and Hf Si oxynitride dielectrics on Ge(100) and Ge(111) substrates are in process, and results will be reported in a future publication.

### 4. Discussion

Thin films, with locally ordered bonding arrangements generated by strain-reducing chemical bonding self-organizations (CBSOs), have been

incorporated into optical, electrical and photo-receptor devices, including thin film and field effect transistors (TFTs and FETs) and phase change optical and electrical memories [12]. This paper identifies qualitative and quantitative differences in the length scales associated with the CBSOs in non-crystalline and nano-crystalline thin film oxide dielectrics for microelectronic applications. This is accomplished through a combination of optical, ultra-violet and X-ray spectroscopy studies, complemented by semi-empirical bond-constraint theory (SE BCT) and ab-initio molecular orbital (MO), in particular symmetry adapted linear combinations (SALCs) of atomic states. There are commonalities between different strain-driven length scales that promote defect reductions critical to device performance in non-crystalline and nano-crystalline films. For materials with the same composition used in both non-crystalline and nano-crystalline thin film devices, spectroscopy results clearly establish a significant discontinuity in length scales ( $\lambda_s$ ) for optimized non-crystalline films,  $\lambda_s < 1$  nm, and nano-crystalline films,  $\lambda_s > 2$  nm. In nano-crystalline films, there two critical size effects: films with nano-grains between about 1.8 and 2.5 nm do not have coherent grain boundaries, but have instead  $\sim 2$  atomic layers of disordered bonding connecting nano-grains; while, films with nano-grains  $> 3$  nm have grain boundaries and also qualitatively different electronic structures and defects/defect precursors.

The importance of chemical bonding self-organizations [17,18], and its role in reducing both bond-strain, and macroscopic strain is the common theme that connects this two seemingly different groups of materials together; the transition metal dielectrics of this paper, and the other device application materials of Ref. 12.

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