Faculty and Staff Publication:

**Sonal Dey, Kandabara Tapily, Steven Consiglio,
Robert D. Clark, Cory S. Wajda, Gert J. Leusink,
Arthur R. Woll, and Alain C. Diebold**

Citation for Final Published Work:

Dey, S., Tapily, K., Consiglio, S. Clark, R. D. Wajda, C. S., Leusink, G. J., ... Diebold, A. C.
(2016). Role of Ge and Si substrates in higher-k tetragonal phase formation and interfacial
properties in cyclical atomic layer deposition-anneal $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2/\text{Al}_2\text{O}_3$ thin film stacks.
Journal of Applied Physics, 120, 125304. doi:10.1063/1.4963166

<http://dx.doi.org/10.1063/1.4963166>

Role of Ge and Si substrates in higher-k tetragonal phase formation and interfacial properties in cyclical atomic layer deposition-anneal $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2/\text{Al}_2\text{O}_3$ thin film stacks

Sonal Dey^{*}, Kandabara Tapily, Steven Consiglio, Robert D. Clark, Cory S. Wajda, Gert J. Leusink, Arthur R. Woll, and Alain C. Diebold

Citation: *Journal of Applied Physics* **120**, 125304 (2016); doi: 10.1063/1.4963166

View online: <http://dx.doi.org/10.1063/1.4963166>

View Table of Contents: <http://aip.scitation.org/toc/jap/120/12>

Published by the American Institute of Physics

Small Conferences. BIG Ideas.

SAVE THE DATE!

3D Bioprinting: Physical and Chemical Processes

May 2–3, 2017 • Winston Salem, NC, USA

Applied Physics Reviews

Role of Ge and Si substrates in higher-k tetragonal phase formation and interfacial properties in cyclical atomic layer deposition-anneal $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2/\text{Al}_2\text{O}_3$ thin film stacks

Sonal Dey,^{1,a)} Kandabara Tapily,² Steven Consiglio,² Robert D. Clark,² Cory S. Wajda,² Gert J. Leusink,² Arthur R. Woll,³ and Alain C. Diebold¹

¹*Colleges of Nanoscale Science and Engineering, SUNY Polytechnic Institute, 257 Fuller Rd., Albany, New York 12203, USA*

²*TEL Technology Center, America, LLC, 255 Fuller Rd., Suite 214, Albany, New York 12203, USA*

³*Cornell High Energy Synchrotron Source (CHESS), Ithaca, New York 14853, USA*

(Received 22 June 2016; accepted 8 September 2016; published online 27 September 2016)

Using a five-step atomic layer deposition (ALD)-anneal (DADA) process, with 20 ALD cycles of metalorganic precursors followed by 40 s of rapid thermal annealing at 1073 K, we have developed highly crystalline $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$ ($0 \leq x \leq 1$) thin films (< 7 nm) on ~ 1 nm ALD Al_2O_3 passivated Ge and Si substrates for applications in higher-k dielectric metal oxide semiconductor field effect transistors below 10 nm technology node. By applying synchrotron grazing incidence x-ray *d*-spacing maps, x-ray photoelectron spectroscopy (XPS), and angle-resolved XPS, we have identified a monoclinic to tetragonal phase transition with increasing ZrO_2 content, elucidated the role of the Ge vs Si substrates in complete tetragonal phase formation (CTPF), and determined the interfacial characteristics of these technologically relevant films. The ZrO_2 concentration required for CTPF is lower on Ge than on Si substrates ($x \sim 0.5$ vs. $x \sim 0.86$), which we attribute as arising from the growth of an ultra-thin layer of metal germanates between the $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$ and $\text{Al}_2\text{O}_3/\text{Ge}$, possibly during the first deposition and annealing cycle. Due to Ge-induced tetragonal phase stabilization, the interfacial metal germanates could act as a template for the subsequent preferential growth of the tetragonal $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$ phase following bottom-up crystallization during the DADA ALD process. We surmise that the interfacial metal germanate layer also function as a diffusion barrier limiting excessive Ge uptake into the dielectric film. An ALD Al_2O_3 passivation layer of thickness ≥ 1.5 nm is required to minimize Ge diffusion for developing highly conformal and textured HfO_2 based higher-k dielectrics on Ge substrates using the DADA ALD process. *Published by AIP Publishing.*

[<http://dx.doi.org/10.1063/1.4963166>]

I. INTRODUCTION

Although hafnia based gate dielectrics have been successfully integrated into very large scale integration (VLSI) technology at the 45 nm node,¹⁻³ continued device scaling introduces a performance bottleneck for Si-based complementary metal oxide semiconductor field effect transistors (MOSFETs).^{4,5} For superior device performance at sub 10 nm nodes, germanium is being considered as an alternate channel material, owing to its intrinsic high mobility (electrons: $3900 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$; holes: $1900 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)⁶ and relative ease of integration into the existing Si-based technology.^{4,7} However, desorption of the native oxide of Ge at a relatively low temperature (~ 675 K) is a major concern and further improvements are required in the physical and chemical processes employed during device fabrication under the scope of the existing technology.^{5,8} In this regard, ultra-thin layers of Al_2O_3 have shown great promise as a defect passivation layer in Ge devices.⁹⁻¹¹ To continue equivalent-oxide-thickness scaling and enhance gate dielectric performance beyond the 10 nm technology nodes, research and development efforts are progressing on two fronts: (1) by introduction of new higher-k

dielectrics via crystal structure engineering, e.g., HfO_2 and ZrO_2 mixtures using unique atomic layer deposition (ALD) schemes, and (2) by integration with high-mobility Ge channels with passivation and performance improving interfacial layers such as Al_2O_3 .⁵

The mixed oxides of HfO_2 and ZrO_2 are promising candidates for higher-k gate dielectrics because they offer the combined benefits of a reasonably wide band gap, adequate conduction, and valence band offset with respect to the channel material, excellent thermal stability, greater controllability of equivalent-oxide-thickness scaling with acceptable leakage current density,^{4,5,12,13} and the possibility of realizing very high dielectric constant ($k > 50$) gate dielectrics by engineering the crystal structure to be stabilized in the higher-k tetragonal or cubic phase.^{14,15} In addition, choice of favorable annealing temperatures, superior ALD processes, and the nature of the semiconductor substrate are critical for improving the interfacial qualities and structural properties of higher-k dielectrics without degradation of the electrical performance of the deposited films.¹⁶ Combining compositional alloying and a cyclical atomic layer deposition-anneal (DADA) process, we have successfully shown the completion of higher-k tetragonal phase formation in $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$ ($0 \leq x \leq 1$) thin films directly deposited on silicon substrates.¹⁷⁻¹⁹

^{a)}Author to whom correspondence should be addressed. Electronic mail: sdey@sunypoly.edu.

Albeit there are numerous reports on physical and electrical characterization of hafnia and zirconia based gate dielectrics,^{4,5,12,13} a systematic study of the effect of the substrate (Ge vs. Si) on the structural and interfacial properties of the ALD dielectric $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$ ($0 \leq x \leq 1$) thin films subjected to a cyclical deposition and annealing scheme has not been reported previously. In this work, we carry out a comparative investigation of the role of interfacial layer and ZrO_2 concentration in higher- k tetragonal phase formation in 100 ALD cycle $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$ ($0 \leq x \leq 1$) thin films on Al_2O_3 passivated Ge and Si substrates using a DADA process. The films are grown in a 5-step DADA process where a 40 s rapid thermal anneal is performed at 1073 K after every 20 cycles. The cycle ratios for the metal-organic precursors tetrakis(ethylmethyamido)hafnium(IV) (TEMAH) and tetrakis(ethylmethyamido) zirconium(IV) (TEMAZ) were varied to obtain a homogeneous compositional spread of HfO_2 and ZrO_2 , respectively.^{17,19,20} The DADA ALD grown films are highly conformal and possess excellent uniformity and control over atomic scale thickness due to the self-limiting surface reaction mechanism inherent in the ALD process.^{16,21,22} The use of the DADA ALD process allowed deposition of highly conformal dielectric films having fiber texture, reduced leakage, and fewer defects. Applying a combination of grazing incidence d -spacing maps (GI-DSMs), x-ray photoelectron spectroscopy (XPS) and angle-resolved XPS (ARXPS), we show that a metal germanate (MGeO_y ; $\text{M} = \text{Hf}, \text{Zr}$) rich interfacial layer (IL) could act as a suitable template for complete tetragonal phase formation (CTPF) with a smaller critical amount of ZrO_2 in $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$ dielectric films grown on Ge substrates. The IL may also act as a barrier to subsequent Ge diffusion up the dielectric stack.

II. EXPERIMENTAL

A. Atomic layer deposition of the thin films

On top of a clean 300 mm Si (100) wafer, a thin buffer layer of graded SiGe was grown followed by the epitaxial growth of approximately 300 nm of Ge as the Ge-substrate. The native oxide of Ge was carefully removed using anhydrous HF and NH_3 gases. Next, ~ 1 nm of Al_2O_3 was atomic layer deposited on both the cleaned Ge and Si substrates using trimethylaluminum (TMA) as the precursor and H_2O as the oxidant. The higher- k dielectric films of $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$ ($0 \leq x \leq 1$) were deposited using a DADA ALD process on top of the Al_2O_3 passivated Si and Ge substrates. Along with H_2O as the oxidant, TEMAH and TEMAZ were used as the precursors for HfO_2 and ZrO_2 atomic layer deposition (ALD), respectively. A total of 20 ALD cycles were carried out at 523 K. One cycle consisted of the following sequence: precursor exposure, inert gas purge, oxidant exposure, and inert gas purge. The varying values of x ($\sim 0, 0.25, 0.33, 0.50, 0.86$, and 1.0) were obtained by varying the cycle ratio of TEMAZ and TEMAH containing steps during each deposition step and were verified by XPS. After the first deposition step of 20 ALD cycles, the films were annealed for 40 s at a temperature of 1073 K after vacuum-transferring the wafers into a rapid thermal annealing chamber connected to the ALD chamber on a common platform. Each deposition

and anneal constituted one step of the DADA scheme. A total of 5 such steps were carried out in order to obtain the 100 ALD cycle DADA $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$ ($x = 0, 0.25, 0.33, 0.50, 0.86$, and 1.0) thin films deposited on ~ 1 nm Al_2O_3 passivated Ge and Si substrates. A total of 12 thin film stacks were prepared for this study.

B. Grazing incidence x-ray diffraction and d -spacing maps

The room temperature grazing incidence x-ray diffraction (GI-XRD) measurements were done at the G2 beamline of the Cornell High Energy Synchrotron Source (CHESS) using x-rays of energy 11.27 keV and 11.24 keV for the films grown on Ge and Si, respectively. The experimental setup and the various motor displacements are shown in the [Appendix](#) (Fig. 4). At the CHESS G2 beamline,²³ the x-ray beam is wide in the horizontal direction (~ 2.0 mm) and narrow (~ 0.2 mm) in the vertical direction giving access to a large diffraction volume which is highly suitable for GI-XRD studies of thin films. The thin films were mounted at the center of a six-circle diffractometer (kappa-style) using a vacuum chuck and initial alignment (i.e., making the film surface parallel to the incident beam) was made using a wall mounted alignment laser. The final alignments for grazing incidence geometry were done using computer controlled motors connected to the kappa-diffractometer such that the x-ray beam was incident at $\sim 0.5^\circ$ and $\sim 0.35^\circ$ for the films grown on Si and Ge, respectively. Using the kappa-diffractometer and a linear detector, we were able to access a large portion of the reciprocal space, while the incident angle and foot-print of the x-ray beam (on the thin films) were kept constant during the sample and detector rotations. A linear detector with 640 channels and fitted with Soller slits was used for collecting the diffracted x-rays such that the beam foot-print-induced-degradation of the resolution of the in-plane scattering angle (at grazing incidence geometry) was limited up to $\sim 0.1^\circ$ (angle of the Soller slits). The detector and the film were rotated by maintaining the Bragg condition between the film rotation (ω) and the horizontal rotation of the linear detector (ν). The linear detector could move in the vertical direction (δ) also while keeping the distance with the center of the kappa-diffractometer (where the sample is mounted) constant. A series of ω - 2ν scans were collected at different values of δ . These motor-scans were converted into grazing-incidence reciprocal space maps (GI-RSMs) by using a Matlab code available at the G2 beamline by taking into account the experimental geometry and the relationships between the various motor displacements²⁴ during the transformation.

For ease of indexing, phase identification, and analysis using scripts written in Python language, the GI-RSMs were converted into grazing-incidence d -spacing maps (GI-DSMs). A representative plot of GI-RSM to GI-DSM conversion is shown in the [Appendix](#) (Fig. 5). A lower angle of incidence ($\sim 0.35^\circ$) was used for the films grown on the Ge substrate in order to minimize the Ge fluorescence (giving a high-background) whose characteristic emission lines are close to the x-ray energy used in this study. Out of all the elements present in our thin films (O, Al, Si, Ge, Zr, and Hf),

only Hf and Ge have some characteristic emission lines close to the x-ray energy used in this study (Table I in the Appendix). As such, most of the grazing incidence maps show some fluorescence background, although the effect is minimized in the case of films not containing Hf or for films deposited on the Si substrate.

The full GI-DSMs and the χ -integrated GI-XRD data after subtraction of a polynomial background for both sets of 100 ALD cycle DADA $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$ ($0 \leq x \leq 1$) films grown on ~ 1 nm Al_2O_3 passivated Si and Ge substrates are discussed in the Appendix (Figs. 6 and 7). Although the full GI-DSMs are found useful for phase identification, a specific portion of the GI-DSMs were used for the quantitative analysis presented in Fig. 1.

C. X-ray photoelectron spectroscopy (XPS) and angle-resolved XPS (ARXPS)

A monochromatic Al K_α x-ray source in conjunction with a hemispherical sector analyzer was used to collect the XPS and ARXPS data, at a base pressure of $\approx 6.0 \times 10^{-9}$ Torr, using a Thermo Scientific Theta ProbeTM system. Energy steps of 0.1 eV and pass energy of 100 eV were used.

FIG. 1. (a) The m - t transition for the $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$ films deposited on Al_2O_3 passivated Si and Ge substrates with increasing ZrO_2 content. The $m\{111\}$ peaks gradually evolve into $t\{111\}$ peak with increasing x . The χ -angle integrated XRD data are fit with Voigt line shapes to calculate (b) the normalized integrated peak area (IPA) ratio and determine the value of x for CTPF in both sets of films.

The XPS and ARXPS spectra were charge corrected with respect to the C 1s peak at 284.8 eV. The ARXPS spectra were measured without tilting the sample using a 16 channel angular dispersive detector over an angular range of $\sim 25^\circ$ to 81° . To minimize the effect of elastic scattering,^{25,26} data up to 60° were used for ARXPS modelling. The data were angle-summed up to 60° in order to obtain the standard XPS spectra. Details of the ARXPS modelling and the tables for binding energy (BE) calculated from XPS are provided in the Appendix.

III. RESULTS AND DISCUSSION

A. Complete tetragonal phase formation (CTPF)

A monoclinic (m) to tetragonal (t) phase transition occurs with increasing amount of ZrO_2 in the DADA $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$ thin-films deposited on Al_2O_3 passivated Si and Ge substrates. The indexing and structure determination of the dielectric films conforming to monoclinic ($P2_1/c$) and tetragonal ($P4_2/nmc$) space groups are presented in detail in the full GI-DSMs in the Appendix. In order to quantify the amount of ZrO_2 required for CTPF in these films, we concentrated on a portion of the GI-DSMs, where certain monoclinic and tetragonal peaks coexist (see Fig. 1(a)). The localization of the Bragg peaks along the χ -axis indicates preferential orientation along certain crystallographic directions. The $m\{111\}$ peaks become weaker and the $t\{111\}$ peaks intensify with increasing ZrO_2 content. In Fig. 1(a), we also show the χ -angle integrated x-ray diffraction (XRD) plots obtained from the respective GI-DSMs.

The m - t transition is accompanied by an increase in the lattice component of the dielectric constant¹³ and expected to increase the overall value of the dielectric constant from $k \sim 16$ in the monoclinic phase to a much larger value in the tetragonal phase (ideally $k \geq 50$).^{14,15,27} The composition dependent m - t phase transition is consistent with Gibbs free energy calculations which show that the contribution of the surface energy term becomes dominant over the bulk energy term for ZrO_2 based films smaller than ~ 7 nm.²⁸ We fitted Voigt line-shapes to the XRD plots in Fig. 1(a) and calculated the normalized integrated peak area (IPA) ratio $[=t^{\text{IPA}}/(t^{\text{IPA}} + m_1^{\text{IPA}} + m_2^{\text{IPA}})]$ in order to quantify the ZrO_2 content required for CTPF, as shown in Fig. 1(b). The m - t transition is first observed at the same value of $x \sim 0.25$ for films grown on Si and Ge. With increasing x , the IPA for the tetragonal peaks increases and that for the monoclinic peaks decreases. The change is more remarkable for films grown on Ge where CTPF is achieved at $x \sim 0.5$ as compared to the films grown on Si where a larger ZrO_2 content ($x > 0.5$ and close to 0.86) is required. As both sets of films are prepared following the same DADA ALD process, we attribute the apparent lowering of ZrO_2 concentration for CTPF in films grown on the Ge substrate to defect mediated thermal diffusion of Ge from the substrate into the Al_2O_3 passivation layer and above. Shibayama *et al.* have shown that a stable aluminum germanate complex could form at the ALD ~ 1 nm $\text{Al}_2\text{O}_3/\text{Ge}$ interface by a low activation energy Ge-diffusion process.²⁹ Since the annealing step during the DADA process on ~ 1 nm Al_2O_3 passivated Ge was done at

1073 K, it is likely that a small fraction of Ge atoms diffused²⁹ onto the top surface of the Al_2O_3 passivation layer. The dangling bonds on those Ge-atoms are expected to be passivated by the O-atoms during the $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$ deposition,³⁰ thus forming a metal germanate rich IL at the interface. Since the presence of Ge is expected to aid the formation of the tetragonal phase in HfO_2 and ZrO_2 dielectrics,^{27,31–33} we speculate that the metal germanate rich IL is in the tetragonal phase and acts as an template³⁴ for CTPF at lower ZrO_2 concentration in films grown on $\text{Al}_2\text{O}_3/\text{Ge}$.

B. XPS results

XPS and ARXPS measurements were applied to study the formation of the metal germanate (MGeO_x ; $\text{M} = \text{Hf}, \text{Zr}$) rich IL in these films. Figs. 2(a)–2(d) show the Hf^{4+} 4f and Zr^{4+} 3d core electron binding energy (BE) regions measured by XPS for the $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$ films deposited on Ge and Si substrates (also see Table II in the Appendix for BE values). Two primary observations from the XPS results are as follows: (1) The BEs of the Hf^{4+} 4f and Zr^{4+} 3d core electrons increase slightly with the ZrO_2 content for films deposited on both types of substrates, and (2) the BEs of the Hf^{4+} 4f and Zr^{4+} 3d core electrons of the films grown on Ge are found to be ~ 0.3 eV higher than the BEs of those deposited on Si. The small increase in BE with x (~ 0.1 eV overall from HfO_2 to ZrO_2 films) can be explained by taking into account the decrease in the M-O bond distances during the m - t transition. An increase in the nearest neighbor oxygens from seven to eight during the m - t transition gives rise to slightly shortened M-O bond distances in the tetragonal phase.³⁵ A shorter M-O bond distance

leads to lesser screening of the electrostatic force between the nucleus and the core electrons and more tightly bound core electrons in the tetragonal phase.^{36,37} The increased BE (by ~ 0.3 eV) for the films deposited on Ge in comparison to the films on Si is explained by considering the second nearest-neighbor effect of Ge^{37–39} which is present in the IL. Assuming the co-existence of the M-O-M (higher- k) and M-O-Ge (IL) type bonding arrangements, the decreased electron donation from the second nearest-neighbor Ge induces a small reduction in the electron density on the M-atom.³⁸ The reduced screening of the core levels of the M-atoms in the IL increases the overall measured BE values of the Zr^{4+} 3d and Hf^{4+} 4f core level electrons for films grown on the Ge substrates.

Fig. 2(e) shows the XPS peak for the Zr^{4+} 3d region with three different processing conditions: BE of Zr^{4+} core electrons for the post-deposition-annealed (PDA) ZrO_2/Ge and DADA $\text{ZrO}_2/\text{Al}_2\text{O}_3/\text{Ge}$ shift towards higher BE side by ~ 0.7 and ~ 0.5 eV with respect to the as-deposited ZrO_2/Ge stack with a Zr^{4+} 3d_{5/2} core electron BE of ~ 182.7 eV. The BE of Ge^{x+} 2p_{3/2} core electrons for the same samples is shown in Fig. 2(f). No XPS signal could be detected in the Ge^{x+} 2p_{3/2} region of the as-deposited ZrO_2 film, indicating that Ge is buried deep in the stack. The BE of Ge^{x+} 2p_{3/2} core electrons for the annealed samples (PDA: ~ 1219.9 eV and DADA: ~ 1219.8 eV) is smaller than the BE of the Ge^{4+} core electrons in GeO_2 (1220.40 ± 0.20 eV; see Table III in the Appendix) but higher than the BE of Ge^0 core electrons (1217.34 ± 0.14 eV; see Table III). Also the intensity of the Ge^{x+} 2p_{3/2} peak for the DADA film is considerably lower than that of the PDA film. This indicates partial suppression of Ge-diffusion by the Al_2O_3 passivation layer, limiting the

FIG. 2. (a)–(d) Binding energies (BEs) of the Hf^{4+} 4f and Zr^{4+} 3d core electrons for DADA $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2/\text{Al}_2\text{O}_3$ on Si and Ge substrates; (e) BE of the Zr^{4+} 3d core electrons for the as dep. and PDA ZrO_2/Ge stacks, and DADA $\text{ZrO}_2/\text{Al}_2\text{O}_3/\text{Ge}$; (f) BE of the Ge^{x+} 2p_{3/2} core electrons for the same stacks in (e). The PDA film in (e) shows the largest shift in BE with respect to the as dep. film due to the presence of a higher fraction of metal germanates in the film. The reduced intensity and the smaller shift in BE of the Ge^{x+} 2p_{3/2} core electrons in the DADA film (with Al_2O_3 passivation layer) indicate that metal germanate formation is limited to the interface.

MGeO_x formation close to the interface such that the BE of the Zr⁴⁺ core electrons for the DADA ZrO₂/Al₂O₃/Ge film is in between the as-deposited and PDA ZrO₂/Ge films. The small decrease in BE for the Ge⁴⁺ for the DADA film (in comparison to the PDA film) is an additional confirmation of MGeO_x IL formation in the DADA samples deposited on Al₂O₃/Ge.

C. Identification of the interfacial layer (IL)

Parallel ARXPS was used to measure the compositional depth profile and determine the position of the IL in the multi-layered gate stack of DADA ZrO₂/Al₂O₃/Ge. Compositional depth profiles are constructed from the ARXPS data using a maximum entropy approach^{40,41} and the results are plotted in Figs. 3(a) and 3(b). Details of the ARXPS modelling are provided in the Appendix. Fig. 3(a) displays the elemental depth profile, indicating that the majority of the Ge^{x+} 2p_{3/2} signal is originating from the IL between the ~1 nm Al₂O₃ and ~6.5 nm of ZrO₂. As shown

in Fig. 3(b), the presence of ~1 nm thick Zr_{0.5}Ge_{0.5}O₂ IL could be deduced from modelling of the ARXPS data (also see the Appendix). The atomistic sketch of Fig. 3(c), although not an exact structural representation, is to be used for visualizing the positions of various elements in the stack. In practice, the IL is expected to be intermixed with the Al₂O₃ passivation layer and a section of the ZrO₂ film close to the interface.

D. Effect of passivation layer thickness on higher-k phase formation

In Figs. 3(d) and 3(e), we show the effect of incorporating different thicknesses of the ALD Al₂O₃ passivation layer in DADA ALD Hf_{1-x}Zr_xO₂/Al₂O₃/Ge (x = 0.25) which is in the mixed phase. The relative intensity of the tetragonal peak is seen to decrease with Al₂O₃ thickness. The normalized IPA ratio for the tetragonal phase is higher for the stack with 5 Å Al₂O₃ due to the presence of a higher percentage of Ge-atoms at the IL which aids the formation of a tetragonal phase.^{27,31-33} With increasing Al₂O₃ thickness, less number

FIG. 3. (a) Compositional depth profile from the ARXPS data for the DADA ZrO₂/Al₂O₃/Ge film showing the presence of Ge at the IL; (b) ARXPS modelling done with Zr_{0.5}Ge_{0.5}O₂ as the IL composition and adventitious carbon (Adv. C) as the charge reference (284.8 eV); (c) for brevity, a simplified atomistic sketch drawn in Vesta⁴² showing the various regions of the stack with the IL sandwiched between the ZrO₂ and the Al₂O₃; for the DADA Hf_{1-x}Zr_xO₂/Al₂O₃/Ge film (x = 0.25), (d) portion of GI-DSM and (e) normalized integrated peak area (IPA) ratio showing suppression of tetragonal phase formation due to reduction in Ge-diffusion with increasing Al₂O₃ thickness.

of Ge-atoms could diffuse into the IL which in turn decreases the strength of the tetragonal component. Since excessive Ge-diffusion across the ~ 1 nm Al_2O_3 passivation layer could lead to increased leakage current,⁶ incorporation of a physically thicker ALD Al_2O_3 passivation layer (≥ 15 Å) is desired for optimal suppression of Ge up-diffusion during the DADA ALD process.

IV. CONCLUSION

Using a 5-step DADA ALD process, we have developed preferentially orientated $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$ ($0 \leq x \leq 1$) films which crystallize in the tetragonal phase for advanced MOSFET applications in which Hf-based higher-k dielectrics are desirable. Complete tetragonal phase formation is achieved with a smaller ZrO_2 content for films grown on ~ 1 nm $\text{Al}_2\text{O}_3/\text{Ge}$ as compared to those on ~ 1 nm $\text{Al}_2\text{O}_3/\text{Si}$. By using a combination of synchrotron GI-DSMs, XPS, and ARXPS, we have shown that an ultra-thin IL of metal germanate is formed just above the passivation layer for the films grown on $\text{Al}_2\text{O}_3/\text{Ge}$. It is proposed that during the first deposition and annealing step at an annealing temperature of 1073 K, Ge thermally diffused across the defect paths in the Al_2O_3 layer⁴³ into the higher-k dielectric, forming a metal germanate rich IL. The M-atoms ($M = \text{Hf}, \text{Zr}$) in the tetragonal structure of MO_2 is surrounded by 8 oxygen atoms, 4 of which are at a shorter distance.³⁵ Thus, replacement of some of the M-atoms by Ge-atoms of smaller ionic radius²⁸ can proceed with minimal lattice distortion, eventually forming a Ge-stabilized tetragonal structure at the IL which could act as a template³⁴ for subsequent bottom-up crystallization¹⁷ of the 100 ALD cycle $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$ films, thus explaining the requirement for a smaller amount of ZrO_2 for films grown on Ge by the DADA ALD process. XPS measured binding energy differences of the Zr^{4+} 3d core electrons support the maximum entropy ARXPS compositional depth profiling which indicates that the IL mostly consists of a network of M-O-Ge type bonds compared to the M-O-M type bonding arrangement in the bulk of the dielectric film. As such, the metal germanate based IL could also act as an efficient barrier³⁹ to prevent further up-diffusion of Ge. Formation of a high quality interfacial layer is essential for enhancing electrical performance of Ge based higher-k metal-oxide-semiconductor devices.^{44–46} Although the DADA process is useful in forming highly textured, tetragonal films expected to be useful in developing higher-k films with less structural defects, the electrical performance is critically dependent on the stability of the passivation and interfacial layers and chemical inter-diffusion in the deposited stack. Incorporation of a physically thicker Al_2O_3 passivation layer (≥ 1.5 nm) provides superior control over Ge-diffusion into the $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$ dielectric film grown via the DADA ALD process on $\text{Al}_2\text{O}_3/\text{Ge}$. The difference in the tetragonal phase formation trends with compositional alloying for the different substrates highlights the importance of understanding the role of the semiconductor substrates and associated mobile species which gives rise to different chemical and structural properties in various processing and integration schemes for high mobility substrates in conjunction with higher-k dielectrics.

FIG. 4. Experimental setup used at the CHESS G2 beamline for grazing incidence x-ray diffraction measurements showing the Huber 6-circle kappa-diffractometer, the 4 motors (ω , ν , δ , and z) used during the measurements, the linear detector, and the sample position.

ACKNOWLEDGMENTS

S.D. thanks TEL Technology Center, America, LLC for funding support. Use of Cornell High Energy Synchrotron Source (CHESS) was supported by the National Science Foundation and the National Institutes of Health/National Institute of General Medical Sciences under NSF award DMR-1332208.

APPENDIX: EXPERIMENTAL SETUP FOR GI-XRD MEASUREMENTS

Figure 4 shows the experimental setup used at the CHESS G2 beamline for GI-XRD and GI-RSM measurements.

FIG. 5. GI-RSM to GI-DSM conversion. The equations on the left are used for the representative GI-RSM to GI-DSM conversion shown at the right. The black and red arrows indicate the positions of certain diffraction spots and how they transform from the GI-RSM to GI-DSM. The lower Q values in the GI-RSM transform to higher d and χ values in the GI-DSM.

TABLE I. Characteristic emission lines for all the elements (O, Al, Si, Ge, Zr, Hf) present in the thin films studied in this work.⁴⁷ All values are in keV.

Element	$K\alpha_1$	$K\alpha_2$	$K\beta_1$	$L\alpha_1$	$L\alpha_2$	$L\beta_1$	$L\beta_2$	$L\gamma_1$
O	0.525	...	...	...	...	...	...	...
Al	1.487	1.486	1.557	...	...	...	...	...
Si	1.740	1.739	1.836	...	...	...	...	...
Ge	9.886	9.855	10.982	1.188	1.188	1.218	...	...
Zr	15.775	15.691	17.668	2.042	2.040	2.124	2.219	2.303
Hf	55.790	54.611	63.234	7.899	7.845	9.023	9.347	10.516

FIG. 6. Grazing incidence d-spacing maps (GI-DSMs) for $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2/\text{Al}_2\text{O}_3/\text{Ge}$. (a)–(f) Representative GI-DSMs and the χ -integrated XRD plots of 100 cycle ALD $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2/\text{Al}_2\text{O}_3/\text{Ge}$ for $0 \leq x \leq 1$. The films gradually transform from lower-k monoclinic phase to higher-k tetragonal phase with increasing value of x . The sharp spots are coming from the substrate (Sub.). The white rectangle shows the region in the map where $m\{111\}$ peaks gradually evolve into $t\{111\}$ with increasing ZrO_2 concentration. This is the same region shown in detail in Fig. 1. The indexing is done according to monoclinic (m: black dotted lines) $P2_1/c$ with $a = 5.127 \text{ \AA}$; $b = 5.175 \text{ \AA}$; $c = 5.316 \text{ \AA}$; $\alpha = 90^\circ$; $\beta = 99.034^\circ$; $\gamma = 90^\circ$ and tetragonal $P4_2/nmc$ (r: red dotted lines) with $a = b = 5.105 \text{ \AA}$; $c = 5.243 \text{ \AA}$; $c/a \sim 1.03$. Complete formation of the tetragonal phase is achieved at a lower ZrO_2 content in this set of films as compared to the films grown on Si substrate.

FIG. 7. Grazing incidence d-spacing maps (GI-DSMs) for $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2/\text{Al}_2\text{O}_3/\text{Si}$. (a)–(f) Representative GI-DSMs and the χ -integrated XRD plots of 100 cycle ALD $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2/\text{Al}_2\text{O}_3/\text{Si}$ for $0 \leq x \leq 1$. The films gradually transform from lower- k monoclinic phase to higher- k tetragonal phase with increasing value of x . The sharp spots are coming from the substrate (Sub.). The white rectangle shows the region in the map where $m\{111\}$ peaks gradually evolve into $t\{111\}$ with increasing ZrO_2 concentration. This is the same region shown in detail in Fig. 1. The indexing is done according to monoclinic (m : black dotted lines) $\text{P}2_1/c$ with $a = 5.127 \text{ \AA}$; $b = 5.175 \text{ \AA}$; $c = 5.316 \text{ \AA}$; $\alpha = 90^\circ$; $\beta = 99.034^\circ$; $\gamma = 90^\circ$ and tetragonal $\text{P}4_2/nmc$ (t : red dotted lines) with $a = b = 5.105 \text{ \AA}$; $c = 5.243 \text{ \AA}$; $c/a \sim 1.03$. Complete formation of the tetragonal phase is achieved at a higher ZrO_2 content in this set of films as compared to the films grown on the Ge substrate.

Figure 5 shows the conversion of GI-RSMs into GI-DSMs and the equations used. The conversion into GI-DSM is useful for indexing and phase identification.

Phase identification from GI-DSM

The monoclinic structure (space group $\text{P}2_1/c$) is refined based on the Joint Committee for Powder Diffraction Standards (JCPDS), powder diffraction file (PDF) No. 780050. The tetragonal structure (space group $\text{P}4_2/nmc$) is refined based on the JCPDS PDF No. 080342. The lattice parameters, derived via Rietveld structure refinement for monoclinic $\text{P}2_1/c$ ($a = 5.127 \text{ \AA}$; $b = 5.175 \text{ \AA}$; $c = 5.316 \text{ \AA}$; $\alpha = 90^\circ$; $\beta = 99.034^\circ$; $\gamma = 90^\circ$) and tetragonal $\text{P}4_2/nmc$

($a = b = 5.105 \text{ \AA}$; $c = 5.243 \text{ \AA}$; $c/a \sim 1.03$) space groups, are in good agreement with previously reported values.^{14,15,19,20} The gradual transition from monoclinic to tetragonal (m - t) phase with increasing ZrO_2 content is evident in these plots. The m - t transition is quantified and better understood (see Fig. 1) by focusing in the region marked by the white rectangle in Figs. 6 and 7. It is worth noting that in a typical XRD experiment using a lab diffractometer with a point detector constrained to move along one axis, most of the observed diffraction spots will not be recorded which makes phase identification of textured films quite difficult and tedious. In this regard, the use of GI-DSMs is extremely useful for structural studies of thin and ultra-thin films.

TABLE II. Binding energy (BE) and full width at half maximum (FWHM) values for the Hf^{4+} 4f and Zr^{4+} 3d core electrons determined after peak-fitting of the XPS data shown in Fig. 2 for the 100 ALD cycle higher-k dielectric films. The estimated maximum uncertainty is ± 0.03 eV for all values reported in the table.

	$\text{Hf } 4f_{5/2}$ (eV)		$\text{Hf } 4f_{7/2}$ (eV)		$\text{Zr } 3d_{3/2}$ (eV)		$\text{Zr } 3d_{5/2}$ (eV)	
	BE	FWHM	BE	FWHM	BE	FWHM	BE	FWHM
x	$\text{Hf}_{1-x}\text{Zr}_x\text{O}_2/\text{Al}_2\text{O}_3/\text{Si}$							
0	18.52	1.07	16.86	1.07	...	...	...	...
0.25	18.54	1.06	16.88	1.06	185.11	1.13	182.76	1.13
0.33	18.56	1.06	16.90	1.06	185.20	1.13	182.80	1.13
0.5	18.61	1.06	16.93	1.06	185.22	1.12	182.83	1.12
0.86	18.65	1.06	16.97	1.06	185.24	1.11	182.85	1.11
1	...	...	...	...	185.27	1.10	182.88	1.10
x	$\text{Hf}_{1-x}\text{Zr}_x\text{O}_2/\text{Al}_2\text{O}_3/\text{Ge}$							
0	18.86	1.27	17.19	1.27	...	...	...	...
0.25	18.89	1.27	17.22	1.27	185.301	1.34	182.91	1.34
0.33	18.91	1.27	17.25	1.27	185.36	1.33	182.96	1.33
0.5	18.94	1.26	17.27	1.26	185.40	1.31	183.02	1.31
0.86	19.08	1.25	17.40	1.25	185.50	1.28	183.11	1.28
1	...	...	...	...	185.52	1.29	183.14	1.29

TABLE III. Binding energies of Hf, Zr, and Ge core electrons (both elemental and oxide forms) and their standard deviations calculated from the values reported in the NIST XPS database till May, 2016.⁴⁸

State of the core electron	Binding energy $\pm$ standard deviation/in eV
$\text{Hf}^0 4f_{7/2}$	14.31 ± 0.05
$\text{Hf}^{4+} 4f_{7/2}$	17.24 ± 0.81
$\text{Ge}^0 3d$	29.21 ± 0.28
$\text{Ge}^{x+} 3d$ ($1 \leq x \leq 2$)	29.50 ± 0.13
$\text{Ge}^{4+} 3d$	32.76 ± 0.73
$\text{Zr}^0 3d_{5/2}$	178.93 ± 0.24
$\text{Zr}^{4+} 3d_{5/2}$	182.47 ± 0.66
$\text{Ge}^0 2p_{3/2}$	1217.34 ± 0.14
$\text{Ge}^{4+} 2p_{3/2}$	1220.40 ± 0.20

XPS and ARXPS: Additional information

In Table II, the binding energies of the Zr^{4+} and Hf^{4+} are shown, as determined from peak-fitting of the XPS data shown in Fig. 3. The measured values are in the expected range for Zr^{4+} and Hf^{4+} binding energies for MO_2 ($\text{M} = \text{Zr}, \text{Hf}$) as determined from the values reported in the NIST database⁴⁸ (see Table III).

Fig. 8 shows the angle-summed XPS plots for Al 2p and O 1s regions along with the relative depth plot (RDP) generated from the ARXPS data for the $\text{ZrO}_2/\text{Al}_2\text{O}_3/\text{Ge}$

stack. The RDP is generated from an algorithm that compares intensity ratios from bulk sensitive (25° – 35°) and surface sensitive (50° – 60°) angular ranges. The signal above 60° is not used because of elastic scattering effects.²⁵ From RDP, the average position of the oxidized Ge in the stack was found to be in between the Al_2O_3 passivation layer and the overlying ZrO_2 dielectric. For the ARXPS modelling, a multi-stack structure with an ultra-thin layer of adventitious carbon, a thin layer of ZrO_2 , an ultra-thin interfacial layer (IL) of zirconium germanate with composition of $\text{Zr}_{0.5}\text{Ge}_{0.5}\text{O}_2$, and an ultra-thin layer of Al_2O_3 was used after taking into consideration the respective inelastic mean free paths (IMFPs) and attenuation lengths from the appropriate NIST database into a multi-stack model using the maximum entropy approach.^{25,40,41,49,50} The elemental depth profiles obtained from the ARXPS modelling are plotted in Fig. 3(a) and show the presence of a germanium rich ultra-thin interfacial layer. The compositional depth profile of Fig. 3(b) clearly shows that this interfacial metal germanate rich layer has formed between the ZrO_2 and the Al_2O_3 passivation layer. As expected, the IL extends into the Al_2O_3 layer and also into the ZrO_2 layer above. The formation of the metal germanate rich IL most likely stops further Ge uptake³⁹ after the first deposition-anneal step in our DADA approach.

FIG. 8. Angle-summed XPS and relative depth plot for the $\text{ZrO}_2/\text{Al}_2\text{O}_3/\text{Ge}$ ($x = 0$) film; the angle summed XPS results for (a) Al 2p and (b) O 1s regions with the O 1s B peak having binding energy appropriate for oxygen in Al_2O_3 ; (c) the relative depth plot calculated from the ARXPS signal showing relative depths of various components from the top surface. The relative depth plot shows that Ge^{x+} is mostly concentrated in the interfacial layer between the higher-k and the Al_2O_3 passivation layer.

- ¹K. Mistry, C. Allen, C. Auth, B. Beattie, D. Bergstrom, M. Bost, M. Brazier, M. Buehler, A. Cappellani, R. Chau *et al.*, *Electron Devices Meet.* **2007**, 247–250.
- ²C. Auth, A. Cappellani, J.-S. Chun, A. Dalis, A. Davis, T. Ghani, G. Glass, T. Glassman, M. Harper, M. Hattendorf *et al.*, *VLSI Technol. Symp.* **2008**, 128–129.
- ³B. Greene, Q. Liang, K. Amarnath, Y. Wang, J. Schaeffer, M. Cai, Y. Liang, S. Saroop, J. Cheng, A. Rotondaro *et al.*, *VLSI Technol. Symp.* **2009**, 140–141, available at <http://ieeexplore.ieee.org/document/5200664>.
- ⁴R. Clark, *Materials* **7**, 2913 (2014).
- ⁵T. Ando, *Materials* **5**, 478 (2012).
- ⁶D. P. Brunco, B. D. Jaeger, G. Eneman, J. Mitard, G. Hellings, A. Satta, V. Terzieva, L. Souriau, F. E. Leys, G. Pourtois, M. Houssa, G. Winderickx, E. Vrancken, S. Sioncke, K. Opsomer, G. Nicholas, M. Caymax, A. Stesmans, J. V. Steenbergen, P. W. Mertens, M. Meuris, and M. M. Heyns, *J. Electrochem. Soc.* **155**, H552 (2008).
- ⁷A. Molle, M. N. K. Bhuiyan, G. Tallarida, and M. Fanciulli, *Mater. Sci. Semicond. Process.* **9**, 673 (2006).
- ⁸K. Prabhakaran, F. Maeda, Y. Watanabe, and T. Ogino, *Appl. Phys. Lett.* **76**, 2244 (2000).
- ⁹S. Ogawa, R. Asahara, Y. Minoura, H. Sako, N. Kawasaki, I. Yamada, T. Miyamoto, T. Hosoi, T. Shimura, and H. Watanabe, *J. Appl. Phys.* **118**, 235704 (2015).
- ¹⁰R. Asahara, I. Hideshima, H. Oka, Y. Minoura, S. Ogawa, A. Yoshigoe, Y. Teraoka, T. Hosoi, T. Shimura, and H. Watanabe, *Appl. Phys. Lett.* **106**, 233503 (2015).
- ¹¹K. Tapily, T. Ngai, R. Clark, D. O'Meara, S. Consiglio, R. Gaylord, C. Wajda, D. Veksler, C. Hobbs, K. Matthews, D. Gilmer, P. Kirsch, and G. Leusink, *ECS Trans.* **61**, 89 (2014).
- ¹²*Materials Fundamentals of Gate Dielectrics*, edited by A. A. Demkov and A. Navrotsky (Springer, Dordrecht, 2005).
- ¹³J. Robertson and R. M. Wallace, *Mater. Sci. Eng. R Rep.* **88**, 1 (2015).
- ¹⁴X. Zhao and D. Vanderbilt, *Phys. Rev. B* **65**, 075105 (2002).
- ¹⁵X. Zhao and D. Vanderbilt, *Phys. Rev. B* **65**, 233106 (2002).
- ¹⁶S. W. Lee, B. J. Choi, T. Eom, J. H. Han, S. K. Kim, S. J. Song, W. Lee, and C. S. Hwang, *Coord. Chem. Rev.* **257**, 3154 (2013).
- ¹⁷R. D. Clark, S. Aoyama, S. Consiglio, G. Nakamura, and G. Leusink, *ECS Trans.* **35**, 815 (2011).
- ¹⁸S. Consiglio, K. Tapily, R. D. Clark, G. Nakamura, C. S. Wajda, and G. J. Leusink, *J. Vac. Sci. Technol., A* **31**, 01A115 (2013).
- ¹⁹K. Tapily, S. Consiglio, R. D. Clark, R. Vasić, E. Bersch, J. Jordan-Sweet, I. Wells, G. J. Leusink, and A. C. Diebold, *ECS Trans.* **45**, 411 (2012).
- ²⁰S. Dey, K. Tapily, S. Consiglio, K.-H. Yu, R. D. Clark, C. S. Wajda, G. J. Leusink, A. R. Woll, and A. C. Diebold, *MRS Adv.* **1**, 269 (2016).
- ²¹R. W. Johnson, A. Hultqvist, and S. F. Bent, *Mater. Today* **17**, 236 (2014).
- ²²J. Niinistö, K. Kukli, M. Heikkilä, M. Ritala, and M. Leskelä, *Adv. Eng. Mater.* **11**, 223 (2009).
- ²³See <http://www.chess.cornell.edu/gline/G2.htm> for description of the beamline (last accessed March 19, 2016).
- ²⁴D.-M. Smilgies, *Rev. Sci. Instrum.* **73**, 1706 (2002).
- ²⁵C. J. Powell and A. Jablonski, *J. Vac. Sci. Technol., A* **19**, 2604 (2001).
- ²⁶K. Kimura, K. Nakajima, T. Conard, and W. Vandervorst, *Appl. Phys. Lett.* **91**, 104106 (2007).
- ²⁷D. Fischer and A. Kersch, *Appl. Phys. Lett.* **92**, 12908 (2008).
- ²⁸J.-H. Ahn and S.-H. Kwon, *ACS Appl. Mater. Interfaces* **7**, 15587 (2015).
- ²⁹S. Shibayama, K. Kato, M. Sakashita, W. Takeuchi, N. Taoka, O. Nakatsuka, and S. Zaima, *Appl. Phys. Lett.* **103**, 082114 (2013).
- ³⁰Y. Kamata, Y. Kamimuta, T. Ino, and A. Nishiyama, *Jpn. J. Appl. Phys., Part 1* **44**, 2323 (2005).
- ³¹D. Tsoutsou, G. Apostolopoulos, S. F. Galata, P. Tsipas, A. Sotiropoulos, G. Mavrou, Y. Panayiotatos, A. Dimoulas, A. Lagoyannis, A. G. Karydas, V. Kantarelou, and S. Harissopoulos, *J. Appl. Phys.* **106**, 024107 (2009).
- ³²D. Tsoutsou, G. Apostolopoulos, S. Galata, P. Tsipas, A. Sotiropoulos, G. Mavrou, Y. Panayiotatos, and A. Dimoulas, *Microelectron. Eng.* **86**, 1626 (2009).
- ³³Y.-H. Wu, M.-L. Wu, J.-R. Wu, and L.-L. Chen, *Appl. Phys. Lett.* **97**, 043503 (2010).
- ³⁴R. Zhang, P.-C. Huang, N. Taoka, M. Yokoyama, M. Takenaka, and S. Takagi, *Appl. Phys. Lett.* **108**, 052903 (2016).
- ³⁵A. A. Demkov, *Phys. Status Solidi B* **226**, 57 (2001).
- ³⁶P. E. R. Blanchard, R. G. Cavell, and A. Mar, *J. Solid State Chem.* **183**, 1477 (2010).
- ³⁷*Hard X-Ray Photoelectron Spectroscopy (HAXPES)*, edited by J. C. Woicik (Springer International Publishing, Cham, 2016).
- ³⁸R. L. Opila, G. D. Wilk, M. A. Alam, R. B. van Dover, and B. W. Busch, *Appl. Phys. Lett.* **81**, 1788 (2002).
- ³⁹S. Van Elshocht, M. Caymax, T. Conard, S. De Gendt, I. Hoflijk, M. Houssa, B. De Jaeger, J. Van Steenbergen, M. Heyns, and M. Meuris, *Appl. Phys. Lett.* **88**, 141904 (2006).
- ⁴⁰A. K. Livesey and G. C. Smith, *J. Electron Spectrosc. Relat. Phenom.* **67**, 439 (1994).
- ⁴¹R. Champaneria, P. Mack, R. White, and J. Wolstenholme, *AIP Conf. Proc.* **683**, 154–159 (2003).
- ⁴²K. Momma and F. Izumi, *J. Appl. Crystallogr.* **44**, 1272 (2011).
- ⁴³J. R. Weber, A. Janotti, and C. G. V. de Walle, *J. Appl. Phys.* **109**, 033715 (2011).
- ⁴⁴A. Toriumi, T. Tabata, C. Hyun Lee, T. Nishimura, K. Kita, and K. Nagashio, *Microelectron. Eng.* **86**, 1571 (2009).
- ⁴⁵M. Caymax, S. Van Elshocht, M. Houssa, A. Delabie, T. Conard, M. Meuris, M. M. Heyns, A. Dimoulas, S. Spiga, M. Fanciulli, J. W. Seo, and L. V. Goncharova, *Mater. Sci. Eng. B* **135**, 256 (2006).
- ⁴⁶P. McIntyre, D. Chi, C. O. Chui, H. Kim, K.-I. Seo, K. Saraswat, R. Sreenivasan, T. Sugawara, F. S. Aguirre-Testado, and R. M. Wallace, *ECS Trans.* **3**, 519 (2006).
- ⁴⁷See <http://www.med.harvard.edu/jpnm/physics/refs/xrayemis.html> for X-ray Emission Lines (last accessed March 19, 2016).
- ⁴⁸A. V. Naumkin, A. Kraut-Vass, S. W. Gaarenstroom, and C. J. Powell, NIST X-Ray Photoelectron Spectroscopy Database, Version 4.1 (2012).
- ⁴⁹S. Tanuma, C. J. Powell, and D. R. Penn, *Surf. Interface Anal.* **20**, 77 (1993).
- ⁵⁰A. Jablonski and C. J. Powell, *Surf. Sci. Rep.* **47**, 33 (2002).