### Ab initio molecular dynamics simulations of properties of a-Al<sub>2</sub>O<sub>3</sub> /vacuum and a-ZrO<sub>2</sub> /vacuum vs a-Al<sub>2</sub>O<sub>3</sub>/Ge(100)(2×1) and a-ZrO<sub>2</sub>/Ge(100)(2×1) interfaces

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The local atomic structural properties of a-Al<sub>2</sub>O<sub>3</sub>, a-ZrO<sub>2</sub> vacuum/oxide surfaces, and a-Al<sub>2</sub>O<sub>3</sub>/Ge(100)(2×1), a-ZrO<sub>2</sub>/Ge(100)(2×1) oxide/semiconductor interfaces were investigated by density-functional theory (DFT) molecular dynamics (MD) simulations. Realistic a-Al<sub>2</sub>O<sub>3</sub> and a-ZrO<sub>2</sub> bulk samples were generated using a hybrid classical-DFT MD approach. The interfaces were formed by annealing at 700 and 1100 K with subsequent cooling and relaxation. The a-Al<sub>2</sub>O<sub>3</sub> and a-ZrO<sub>2</sub> vacuum/oxide interfaces have strong oxygen enrichment. The a-Al<sub>2</sub>O<sub>3</sub>/Ge interface demonstrates strong chemical selectivity with interface bonding exclusively through Al–O–Ge bonds. The a-ZrO<sub>2</sub>/Ge interface has roughly equal number of Zr–O–Ge and O–Zr–Ge bonds. The a-Al<sub>2</sub>O<sub>3</sub>/Ge junction creates a much more polar interface, greater deformation in Ge substrate and interface intermixing than a-ZrO<sub>2</sub>/Ge consistent with experimental measurements. The differences in semiconductor deformation are consistent with the differences in the relative bulk moduli and angular distribution functions of the two oxides. © 2009 American Institute of Physics. [DOI: 10.1063/1.3078035]

### I. INTRODUCTION

The rapid scaling of complementary metal oxide semiconductor (CMOS) technology requires substituting the traditional gate oxide, SiO<sub>2</sub>, with high-*k* dielectrics, which can maintain the same capacitance with much lower leakage current. Amorphous aluminum and zirconium oxides (*a*-Al<sub>2</sub>O<sub>3</sub> and *a*-ZrO<sub>2</sub>) are leading candidates for such high- $\kappa$  gate oxide materials. Ge is one of a few semiconductors that offer significantly higher hole mobility than silicon and is being extensively investigated for *p*-channel high- $\kappa$  metal-oxide semiconductor field-effect transistor (MOSFETs).<sup>1–3</sup>

Although amorphous oxides are exclusively employed as commercial gate oxides in MOSFET devices, nearly all reports of density-functional theory (DFT) simulations of high- $\kappa$  oxide-semiconductor interfaces are limited to crystalline oxides.<sup>4–9</sup> The DFT studies that simulate amorphous high-k gate oxides on silicon contain an a-SiO<sub>2</sub> interlayer, thereby removing direct high-k amorphous oxidesemiconductor bonds.<sup>10</sup> Amorphous oxide-semiconductor interfaces are expected to be superior to crystalline oxidesemiconductor interfaces due to the lack of lattice mismatch that can induce a high density of interface defects. Despite their chemical composition similarity to crystalline phases, amorphous Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub> demonstrate quite different microstructures, coordination distributions, and atomistic chemical environments. Whereas many previously reported simulations of oxide-semiconductor interfaces were limited to the structural relaxation of artificially built systems, in this

study MD is applied at finite temperatures to provide the amorphous oxide/semiconductor stacks with enough freedom to evolve to the most realistic state.

### II. GENERATION OF AMORPHOUS Al<sub>2</sub>O<sub>3</sub> AND ZrO<sub>2</sub> SAMPLES

Amorphous a-Al<sub>2</sub>O<sub>3</sub> and a-ZrO<sub>2</sub> samples were generated by applying a hybrid "melt and quench" technique that employed classical molecular dynamics (MD) annealing followed by DFT annealing of the classical amorphous sample. Classical MD simulations were performed by a Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS),<sup>11</sup> expanded by well-tested empirical potentials for  $Al_2O_3$  (Ref. 12) and  $ZrO_2$ .<sup>13</sup> All DFT simulations were performed with the Vienna ab initio simulation package (VASP) (Refs. 14 and 15) using projector augmented-wave (PAW) pseudopotentials (PPs) (Refs. 16 and 17) and the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional.<sup>18,19</sup> The choice of PBE functional and PAW PP was validated by parametrization runs demonstrating good reproducibility of experimental lattice constants, bulk moduli, and formation energies for bulk crystalline Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, Al, Zr, and Ge.

The a-Al<sub>2</sub>O<sub>3</sub> and a-ZrO<sub>2</sub> samples were stoichiometric and consisted of 100 and 96 atoms, respectively. The classical MD generation sequence began with a high-temperature annealing at 5000 K from a low-density ordered oxide phase (Fig. 1). The low-density phase was formed by rescaling the periodic boundary condition (PBC) box size and oxide sample along every direction by a factor of 1.5 compared to the box size at classical amorphous density. High-

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FIG. 1. (Color online) Hybrid classical-DFT MD generation sequence of a-Al<sub>2</sub>O<sub>3</sub> and a-ZrO<sub>2</sub> samples. Stages: (a) low- $\rho$  oxide; (b) high-T annealing at low- $\rho$ ; (c) density rescaling (low  $\rho \rightarrow$  normal  $\rho$ ); (d) high-T annealing at normal- $\rho$ ; (e) cooling to RT; (f) equilibration at RT; (g) density rescale: classical $\rightarrow$  DFT; (h) annealing below melting T; (i) cooling to 0 K; (j) relaxation.

temperature annealing at low density provided very good oxide intermixing and completely erased the original ordered geometry. After annealing at low density, the sample was homogeneously and instantaneously rescaled back to the normal oxide density and annealed again at 5000 K. (The method of selecting the normal amorphous oxide density is explained below.) Afterwards, the melt was linearly cooled to room temperature, passing the amorphization point, and thermally equilibrated (Fig. 1).

The properties of the classically generated a-Al<sub>2</sub>O<sub>3</sub> and a-ZrO<sub>2</sub> samples are sensitive to annealing time at low density and cooling rate. To account for this, these two parameters were varied to give 24 different preparation sequences with 24 different final amorphous samples for each sample type.

The amorphous classical samples were quantified via their radial-distribution function (RDF) main peak positions and full widths at half maximum (FWHM), average nearest neighbor numbers, nearest neighbor distributions, and the calculated neutron scattering static structural factor. The RDF functions were calculated according to Eq. (1) and averaged over 2001 structure snapshots at 10 fs increments, where  $\rho_{\beta} = N_{\beta}/V$  is the number density of species  $\beta$ , and  $N_{\beta}$  is the total number of  $\beta$  atoms.<sup>20</sup>

$$g_{\alpha\beta}(r) = \frac{\langle n_{\alpha,\beta}(r, r + \Delta r) \rangle}{4\pi r^2 \rho_{\beta} \Delta r}.$$
 (1)

The average nearest neighbor number  $n_{\alpha\beta}(R)$  [Eq. (2)] can be obtained by integrating the corresponding RDF curve up to the cutoff radius *R*, which is the position of the first minimum after the main RDF peak.

$$n_{\alpha\beta}(R) = 4\pi\rho_B \int_0^R g_{\alpha\beta}(r)r^2 dr.$$
 (2)

The neutron scattering static structure factors  $(S_N(q))$  [Eq. (3)] are obtained from the partial static structure factors  $(S_{\alpha\beta}(q))$  [Eq. (4)], which are calculated from RDF curves  $g_{\alpha\beta}(r)$  [Eq. (1)], where  $b_{\alpha}$  is the coherent neutron scattering length of species  $\alpha$  ( $b_{\rm Al}=0.3449 \times 10^{-4}$  Å,  $b_{\rm O}=0.5805 \times 10^{-4}$  Å) (Ref. 20) and  $c_{\alpha(\beta)}=N_{\alpha(\beta)}/N$  is the concentration of  $\alpha(\beta)$  species.<sup>20</sup>



FIG. 2. Nearest neighbor distribution of (a) our classical a-Al<sub>2</sub>O<sub>3</sub> sample vs a larger scale classical sample from Ref. 20. Cutoff radius is 2.2 Å. (b) our DFT annealed a-ZrO<sub>2</sub> sample vs DFT generated sample from Ref. 23. Cutoff radius is 3 Å.

$$S_{N}(q) = \frac{\sum_{\alpha\beta} b_{\alpha} b_{\beta} (c_{\alpha} c_{\beta})^{1/2} [S_{\alpha\beta}(q) - \delta_{\alpha\beta} + (c_{\alpha} c_{\beta})^{1/2}]}{(\sum_{\alpha} b_{\alpha} c_{\alpha})^{2}}, \quad (3)$$
$$S_{\alpha\beta}(q) = \delta_{\alpha\beta} + 4\pi\rho (c_{\alpha} c_{\beta})^{1/2} \int_{0}^{R} r^{2} [g_{\alpha\beta}(r) - 1]$$
$$\times \frac{\sin(qr)}{qr} \frac{\sin(\pi r/R)}{\pi r/R} dr. \quad (4)$$

Since the available experimental information on the a-Al<sub>2</sub>O<sub>3</sub> and a-ZrO<sub>2</sub> microstructures is limited, both experimental and selected simulation data<sup>20–26</sup> were used as reference properties. For a-Al<sub>2</sub>O<sub>3</sub>, the classically simulated and well-tested amorphous sample was used as the reference state for the classical MD stage,<sup>20</sup> while for a-ZrO<sub>2</sub>, a DFT generated sample<sup>22–24</sup> was used as the reference state, resulting in the introduction of a small variation in the sample selection procedure.

Of the 24 classical *a*-Al<sub>2</sub>O<sub>3</sub> samples, the most realistic sample, as quantified by RDF main peak positions and FWHMs, average nearest neighbor numbers, nearest neighbor distributions, and the calculated neutron scattering static structural factor, was the sample that had been classically prepared by annealing at 5000 K for 350 ps at low ( $\sim$ 0.9 g/cm<sup>3</sup>) density, instantaneously rescaled with the PBC box to the normal density of 3.20 g/cm<sup>3</sup> (see comment below) and annealed for 400 ps, linearly cooled to RT for



FIG. 3. (Color online) RDF curves for the a-Al<sub>2</sub>O<sub>3</sub> sample generated by classical MD.

100 ps and thermally equilibrated at RT for 100 ps (Fig. 1). During  $Al_2O_3$  high-T (5000 K) annealing at low density, the final average atom displacement was 7.6 Å or  $\sim$ 70% of the smallest PBC lattice vector (11.0 Å). During the subsequent normal density high-T  $Al_2O_3$  annealing, the average atom displacement was 5.1 Å or  $\sim$ 65% of the smallest lattice vector (7.8 Å). The total velocity integration over time indicated an absence of oxide correlated macroscopic motion through PBC boundaries. The high values of average atomic displacement during high-T annealing phases are consistent with a high degree of melt intermixing. Note that these values may be a slight underestimate of the real atom displacements since some atoms pass the whole PBC box. Although sample vaporization can happen during low-density high-T annealing phase, vaporization provides good sample intermixing and has no significant effect on final sample properties; the final sample properties are mainly affected by the amorphization processes during cooling phase.

Amorphous Al<sub>2</sub>O<sub>3</sub> can be stable over a wide range of densities. Experimental measurements report stable amorphous Al<sub>2</sub>O<sub>3</sub> structures with a  $3.05-3.40 \text{ g/cm}^3$  density range,<sup>27,28</sup> while classical and DFT computer simulations demonstrate successful generation at 3.0-3.3 g/cm<sup>3</sup>.<sup>20,29,30</sup> The classical density of the a-Al<sub>2</sub>O<sub>3</sub> sample in this study was chosen to be consistent with previous classical simulations of a-Al<sub>2</sub>O<sub>3</sub> that correlated well with experimental properties.<sup>20,21</sup> The selected a-Al<sub>2</sub>O<sub>3</sub> classical sample is in good agreement with MD simulated nearest neighbor distributions, RDF main peak positions (Figs. 2 and 3, Table I) and neutron scattering static structure factors reported by Gutierrez and Johansson<sup>20</sup> as well as to experimentally measured bond lengths, and neutron scattering static structure factors.<sup>21</sup> Our simulated sample contains moderate deviations in the average coordination numbers when compared to



FIG. 4. (Color online) (a) a-Al<sub>2</sub>O<sub>3</sub> and (b) a-ZrO<sub>2</sub> samples after DFT annealing. Al dark blue, Zr: light blue, O: red.

the reference samples<sup>20,21</sup> since our sample has only 100 atoms whereas the sample in Ref. 20 consisted of 1800 atoms and the sample from Ref. 21 was macroscopic. Furthermore, the experimental coordination distribution and average coordination numbers reported earlier were obtained from experimental x-ray and neutron diffraction curves by the reverse Monte Carlo technique, which could potentially introduce some ambiguity and statistical error in the obtained values.<sup>21</sup>

To match the DFT amorphous density, the most realistic classical a-Al<sub>2</sub>O<sub>3</sub> sample was homogeneously rescaled from the classical  $(3.20 \text{ g/cm}^3)$  to the DFT density  $(3.26 \text{ g/cm}^3)$ resulting in a sample size of  $\sim 11.6 \times 11.6 \times 7.8$  Å. The rescaled sample was then DFT annealed at 1500 K for 1000 fs with a 1.0 fs time step, cooled to 0 K for 200 fs, and relaxed at fixed volume to a value below the specified 0.01 eV/Å force tolerance level [Figs. 1 and 4(a)]. The stress tensor components of the DFT annealed amorphous sample were analyzed to verify the absence of any significant internal hydrostatic pressure. The goal of DFT annealing is to provide adjustment to the more accurate DFT force field without complete melting the initial rescaled classical sample used as a first approximation. Since the DFT annealing was performed at constant volume at the amorphous density (which is considerably lower than the crystalline density) and for a limited time ( $\sim 1$  ps), recrystallization processes were prevented as verified by the final RDF curves being consistent with an amorphous state. To determine the ratio of classical and DFT density, a separate classical a-Al<sub>2</sub>O<sub>3</sub> sample was DFT annealed using the same procedure and. subsequently, relaxed at variable volume. The electronic structure analysis of the DFT annealed and relaxed a-Al<sub>2</sub>O<sub>3</sub> bulk sample indicates a bandgap of 3.80 eV that is free from any defect states, agreeing well with a previously reported DFT bandgap of 3.77 eV.<sup>29</sup> Due to the wider coordination distribution in amorphous samples compared to crystalline

TABLE I. RDF peak maxima and average nearest neighbor numbers for our classical MD a-Al<sub>2</sub>O<sub>3</sub> sample vs a large-scale reference classical MD sample (Ref. 20) and experimental data (Ref. 21).

	Our sample		Simulations		Experiment	
	RDF	$n_{\alpha\beta}$	RDF	$n_{lphaeta}$	RDF	$n_{\alpha\beta}$
Al–O	1.77	4.23	1.76	4.25	1.8	4.1
0–0	2.82	10.66	2.75	9.47	2.8	8.5
Al–Al	3.07	6.98	3.12	8.26	3.2	6.0

ones, our amorphous sample bandgap is lower than the DFTcalculated crystalline  $Al_2O_3$  bandgap (~6.0 eV).<sup>29,31</sup> The angular distribution function (ADF) of our sample demonstrates strong correlation to the previously reported values.<sup>20</sup> Gutierrez and Johansson reported O–Al–O peak at 104° versus 102° for our sample.<sup>20</sup> The Al–O–Al ADF presented in Ref. 20 demonstrates peak at ~120° versus 122° for our sample. The small deviation of our angular distribution data from Ref. 20 can be explained by the fact that Ref. 20 reports upon a classically annealed sample, while our sample was produced by sequential classical and DFT annealing, which introduced the more accurate DFT force field at the end of the simulations.

The classical models of a-ZrO<sub>2</sub> oxide were prepared in a batch of 24 different samples with a density of  $4.71 \text{ g/cm}^3$ . This model follows the same general procedure used for the a-Al<sub>2</sub>O<sub>3</sub> system but with different annealing/cooling times (Fig. 1). The classical amorphous density was calculated from the DFT amorphous density (see comment below) and classical-to-DFT density correction ratio. Since the amount of experimental microstructure data on a-ZrO<sub>2</sub> is limited and often varies with the sample preparation technique, both published DFT simulations as well as experimental measurements were used as reference sample properties.<sup>22-26,32,33</sup> The most realistic classical a-ZrO2 sample was generated by annealing at 5000 K at low density ( $\sim 1.4 \text{ g/cm}^3$ ) for 500 ps, instantaneously rescaling the PBC box to the normal classical density of 4.71 g/cm<sup>3</sup>, annealing for 500 ps, linearly cooling to RT for 100 ps, and thermally equilibrating at RT for 100 ps. During  $ZrO_2$  high-T (5000 K) annealing at low density, the final average atom displacement was 7.9 Å or  $\sim$ 53% of the smallest PBC lattice vector. At the normal density high-T  $ZrO_2$  annealing, the average atom displacement was 5.46 Å or  $\sim$ 54% of the smallest lattice vector. The high values of average atomic displacement during high-T annealing phases are consistent with a high degree of the melt intermixing. Note, these values may be a slight underestimate of the real atom displacement since some atoms pass the whole PBC box.

Since previous DFT simulations reported realistic amorphous a-ZrO<sub>2</sub> structures for a density range between 4.86 and 5.32 g/cm<sup>3</sup>,<sup>22,23</sup> a relatively low DFT sample density value (4.90 g/cm<sup>3</sup>) was selected to minimize the risk of sample recrystallization during DFT annealing and cooling. The sizes of the DFT a-ZrO<sub>2</sub> samples were  $\sim 11.58$  $\times 11.58 \times 10.0$  Å, equivalent to the Ge(100) slab surface area. Since the a-ZrO<sub>2</sub> reference sample microstructure was DFT generated, the three classical samples demonstrating the least deviation of nearest neighbor distribution from the reference sample were selected, rescaled to a DFT density of  $4.90 \text{ g/cm}^3$ , and DFT annealed at 2800 K for 1000 fs, cooled to 0 K for 200 fs and relaxed at fixed volume to a 0.01 eV/Å force tolerance level (Fig. 1).<sup>23</sup> The DFT amorphous oxide annealing was performed at fixed low amorphous density for a limited time interval ( $\sim 1$  ps) effectively preventing sample recrystallization as proven by the RDF curves and nearest neighbor distribution. These three samples were analyzed to determine their final nearest neighbor distributions; the closest match to the reference sample was selected and thoroughly tested [Figs. 2(b) and 4(b)]. In addition to the good agreement between the nearest neighbor distributions of the selected sample and the reference one<sup>23</sup> [Fig. 2(b)], the selected sample also indicates a good correlation of its RDFs with that of the reference sample. The Zr–O RDF main peak is located at 2.1 Å with a Zr–O length distribution primarily in the 2.0–2.3 Å interval versus previously reported intervals of 2.04–2.25 Å.<sup>22–24</sup> The Zr–Zr and O–O RDF main peaks are located at 3.5 and 2.8 Å, respectively. The stress tensor components of the selected DFT annealed *a*-ZrO<sub>2</sub> amorphous sample were analyzed to verify the absence of significant internal hydrostatic pressure.

The DOS and bandgap analysis is an important test since it can screen out defective samples with states in the bandgap. The selected a-ZrO<sub>2</sub> sample has a bandgap of  $\sim$ 2.7 eV free from defect states in comparison with previously reported amorphous ~3.2 eV (DFT,  $\rho$ =5.32 g/cm<sup>3</sup>), ~3.4 eV (DFT,  $\rho = 4.86 \text{ g/cm}^3$ ) and experimental 4.7 eV (Refs. 23-26) values. This discrepancy with experiment is mainly due to the standard DFT bandgap underestimation caused by an inadequate description of the DFT exchange interaction. The DFT sample in Ref. 24 with the  $\sim$ 3.2 eV bandgap was prepared at a different density (5.32 g/cm<sup>3</sup> versus our 4.90 g/cm<sup>3</sup>), using a different generation technique (ART versus our DFT MD), and with a different code [LCAO code (SIESTA) versus a plane-wave code (VASP)]. The DFT sample in Ref. 23 with a bandgap of  $\sim$  3.4 eV was generated by DFT MD at a time scale that was  $\sim$ 55 times shorter than our combined classical-DFT time scale of 1201 ps and had a cooling rate approximately times steeper than in our runs. The problem of all MD atomistic simulations is that the computationally affordable cooling rate is much higher than the cooling rate in real experiments. Performing the amorphization at too high cooling rate can lead to a less realistic sample, since too fast cooling can freeze the liquid state instead of providing the system with enough time for proper amorphization. Therefore, decreasing of the simulated cooling rate actually makes amorphization simulations more realistic. The significantly longer time scale and lower cooling rate used in our runs lead to better intermixing and more extensive and realistic amorphization. Since passage from the crystalline to amorphous phase typically decreases the bandgap, the smaller value of our sample bandgap can be attributed to our longer run time scale and lower cooling rate.29

### **III. OXIDE/Ge INTERFACIAL BONDING SIMULATIONS**

The 64-atom Ge(100)(2×1) substrate was built from a  $2 \times 2 \times 2$  Ge supercell with the DFT optimized lattice constant. The bottom three layers were fixed in the bulk positions and saturated by H atoms. The rest of the slab was relaxed below the 0.01 eV/Å force tolerance level to form the Ge(100)(2×1) surface reconstruction with an ~11.58 × 11.58 × 10.4 Å slab size. To satisfy periodic boundary conditions, the DFT relaxed oxide sample size perfectly matches the DFT relaxed Ge surface area.

The DFT annealed oxide samples  $(a-Al_2O_3 \text{ and } a-ZrO_2)$  were cleaved along the *X*-*Y* plane parallel to the oxide-



FIG. 5. (Color online) General DFT preparation sequence for a-Al<sub>2</sub>O<sub>3</sub>/Ge and a-ZrO<sub>2</sub>/Ge interfaces. Stages: (a) initial relaxation (~30 steps); (b) annealing (~1000 fs); (c) cooling to 0 K (~200 fs); (d) final relaxation (~500–1500 steps); (e) final relaxation at extended *K*-point mesh (~50 steps).

semiconductor interface and periodic boundary conditions were truncated by adding  $\sim 12$  Å of vacuum over the samples. The technique of cleaving an oxide sample before bonding is similar to the approach of Broqvist *et al.*<sup>10,34</sup> The cleavage planes were chosen to provide a roughly equal number of metal and oxygen atoms at the bottom surface. Each cleaved amorphous oxide slab was placed on the relaxed  $Ge(100)(2 \times 1)$  surface at an interfacial distance so that the initial Al-Ge or Zr-Ge pair lengths were equal to approximately 0.5–0.75 of their empirical equilibrium distance. The oxide sample was not relaxed after surface cleavage prior to stacking on Ge in order to provide a chemically reactive surface with dangling bonds for contact with Ge. Conversely, the upper surface of the oxide was passivated by H atoms having  $\sim 12$  Å of vacuum to avoid spurious interactions through periodic boundary conditions. In contrast to other published DFT-MD oxide/semiconductor studies, we use models with one oxide/semiconductor interface and a vacuum layer since the supercell model with two oxide/ semiconductor interfaces and no vacuum might unphysically restrict atomic migration to/from the oxide/semiconductor interface in the thin oxide film ( $\sim 10$  Å).<sup>10,34</sup> In addition, the presence of a vacuum layer over the oxide allows for the complete relaxation of the interfacial oxide-semiconductor height and any possible residual stresses in the amorphous sample induced by bonding to the semiconductor. To compensate for spurious electric fields induced by PBC for this type of system, a dipole correction was applied.<sup>14,15,35</sup>

After oxide/semiconductor stacking, the whole Ge slab was fixed in space while the oxide was partially relaxed for  $\sim$ 20–30 conjugate-gradient (CG) relaxation steps. The duration of this initial relaxation was systematically determined by performing longer (~150 CG steps) relaxation run which showed that  $\sim 20-30$  CG steps were sufficient to reach the optimal interface height, thereby releasing initial artificial stresses and allowing the oxide to conform to the nonplanar reconstructed Ge(100)(2  $\times$  1) topography. After the  $\sim$ 20–30 CG steps of initial partial relaxation with frozen Ge, the Ge atoms were unfixed except for the three bottom layers and the whole system was annealed at 700 or 1100 K for 1000 fs with 1.0 fs time steps, cooled to 0 K for 200 fs, and finally relaxed below a 0.05 eV/Å force tolerance level (Fig. 5). The system was annealed at two different temperatures (700 and 1100 K) to investigate the effects of annealing temperature on interface properties and to evaluate possible influences of increased annealing time scale, which can be estimated by the faster kinetics at high temperature. Since the PBC box is large and the system runs included  $\sim 200$  atoms and  $\sim$ 2500 CG/MD steps, the initial relaxation, annealing, cooling, and final relaxation were performed with a 2 K-point irreducible mesh to obtain acceptable computational efficiency. After the final relaxation, the K-point set was expanded to a  $3 \times 3 \times 1$  mesh, and the system was tuned by another relaxation run. Although expanding the K-point set had no visible effect on the system geometry and required only  $\sim 30-50$  CG steps to relax below the 0.05 eV/Å force tolerance level, it could improve the electronic structure. The process of annealing, cooling, and relaxing the oxide/ semiconductor stack provides unique microscopic insight into the interface evolution and the final microstructure (Figs. 6 and 7).

### IV. VACUUM/OXIDE a-Al<sub>2</sub>O<sub>3</sub> AND a-ZrO<sub>2</sub> INTERFACES

The amorphous bulk samples (Fig. 4) were used to generate vacuum/oxide a-Al<sub>2</sub>O<sub>3</sub> and a-ZrO<sub>2</sub> interfaces (Fig. 8) to provide a comparison to the oxide/semiconductor interfaces. For the bulk amorphous samples, the periodic boundary condition box was extended in the Z-direction by adding  $\sim$ 15.0 Å of vacuum space thereby creating two unrelaxed surfaces. The bulk cleavage plane was chosen to provide a roughly equal number of metal and oxygen atoms on each cleaved surface. The cleaved a-Al<sub>2</sub>O<sub>3</sub> slab was annealed at 1500 K for 1000 fs with 1.0 fs time steps, cooled to 0 K for 200 fs, and relaxed to the ground state with a 0.05 eV/Å force tolerance level. The cleaved a-ZrO<sub>2</sub> slab was annealed, cooled, and relaxed similarly except the annealing temperature was 2800 K (Fig. 8). The experimental melting temperature for Al<sub>2</sub>O<sub>3</sub> is 2326 K, however, since melting temperatures in DFT simulations can differ from experimental ones and since a reliable DFT melting temperature for a-Al<sub>2</sub>O<sub>3</sub> is not available, an overcautious temperature of 1500 K was used for DFT MD annealing of the a-Al<sub>2</sub>O<sub>3</sub> sample.<sup>36</sup> The a-ZrO<sub>2</sub> was previously thoroughly investigated by DFT MD, reporting signs of disorder at 3000 K, and definite melting at 4000 K;<sup>22-24</sup> therefore an annealing temperature of 2800 K could be used for a-ZrO<sub>2</sub> even though it was higher than the a-Al<sub>2</sub>O<sub>3</sub> DFT annealing temperature employed in this study. After annealing and relaxation, the slabs were analyzed to verify their amorphous state. Although real oxide-vacuum interfaces are likely to be OH terminated, the oxide-vacuum interfaces were not terminated with OH to facilitate understanding the influence of semiconductor bonding to the oxide surface compared to the surface of the same oxide without any termination. The current research was intended to investigate and compare fundamental properties of  $a-Al_2O_3/Ge$ , a-ZrO<sub>2</sub>/Ge, and vacuum/a-Al<sub>2</sub>O<sub>3</sub>, vacuum/a-ZrO<sub>2</sub> interfaces, which have not been theoretically investigated before, in the absence of interface absorbates such as OH or N.



### a-Al<sub>2</sub>O<sub>3</sub>/Ge(100)

FIG. 6. (Color) a-Al<sub>2</sub>O<sub>3</sub>/Ge(100)(2×1) interfaces annealed at 700 and 1100 K. Al: blue, O: red, Ge: green, H: white. Note that after final relaxation the interfaces are dominated by O–Ge bonds and the Ge substrate is distorted.

### V. RESULTS AND DISCUSSION

It is very informative to compare structural properties of a-Al<sub>2</sub>O<sub>3</sub>/Ge and a-ZrO<sub>2</sub>/Ge interfaces with vacuum/oxide a-Al<sub>2</sub>O<sub>3</sub> and a-ZrO<sub>2</sub> ones.

## A. Chemical segregation and interfacial dipoles at the oxide/semiconductor and vacuum/oxide interfaces

The DFT annealing of vacuum/*a*-Al<sub>2</sub>O<sub>3</sub> surfaces reveals a pronounced interface chemical segregation with Al atoms migrating into the bulk and O atoms migrating to the surface to create O surface capping [Fig. 8(a)]. This phenomenon of oxygen enrichment of oxide/vacuum interfaces was previously reported for classical MD simulations of the vacuum/*a*-Al<sub>2</sub>O<sub>3</sub> interfaces,<sup>30</sup> and by first-principle simulations of the (0001) interfaces of  $\alpha$ - and (001) interfaces of crystalline  $\kappa$ -alumina with vacuum.<sup>37,38</sup> The surface segregation at the vacuum/*a*-Al<sub>2</sub>O<sub>3</sub> interface can be explained by the different geometries of O and Al bonds. In *a*-Al<sub>2</sub>O<sub>3</sub>, bulk Al atoms predominantly have four or five nearest neighbors (Fig. 2). The Al atom located at the oxide-vacuum interface would likely have a lower number of neighbors thereby increasing the total energy of the system. The O atoms predominantly have only two or three neighbors in the *a*-Al<sub>2</sub>O<sub>3</sub> bulk (Fig. 2); therefore, they will more likely accommodate bonding at the vacuum/oxide interface without significantly changing the total energy.

The *a*-Al<sub>2</sub>O<sub>3</sub>/Ge interfaces annealed at 700 and 1100 K demonstrate very similar interface oxygen enrichment compared to the vacuum/*a*-Al<sub>2</sub>O<sub>3</sub> interface (Fig. 6). For *a*-Al<sub>2</sub>O<sub>3</sub>/Ge interfaces, oxygen atoms migrate to the semiconductor interface and Al atoms migrate into the bulk oxide resulting in interfacial bonding exclusively through Al–O–Ge bonds with no or very few O–Al–Ge bonds.<sup>39</sup> This O-rich bonding is present even during the high-temperature annealing stage [Figs. 6 and 9(a)]. The interface segregation occurs during the first ~100 fs (10% of the whole annealing time), indicating the DFT time scale used is sufficient to observe this phenomenon (Fig. 6). Increasing the interfacial annealing temperature from 700 to 1100 K has no effect on this interface chemical migration.

Interfacial bonding exclusively through Al–O–Ge bonds can result in strong interface polarity; this is not a desired characteristic as significant charge transfer has a negative impact on device performance. To verify and quantify this effect, a Bader charge analysis was performed.<sup>40,41</sup> The Bader charge analysis indicates that for the a-Al<sub>2</sub>O<sub>3</sub>/Ge interfaces annealed at 700 and 1100 K, the Ge atoms bonded to O lose, on average, about 0.7–1.0 |e| of atomic charge



FIG. 7. (Color) a-ZrO<sub>2</sub>/Ge(100)(2×1) interfaces annealed at 700 and 1100 K. Zr: light blue, O: red, Ge: green, H: white. Note that after final relaxation, there are both Zr–O–Ge and O–Zr–Ge bonds and the Ge substrate has low distortion.

(Fig. 6). To investigate the total charge transfer from the Ge substrate into the *a*-Al<sub>2</sub>O<sub>3</sub> bulk through the semiconductor/ oxide interface, the total Bader atomic charge was summed up over all Ge atoms and bottom passivating H's in the *a*-Al<sub>2</sub>O<sub>3</sub>/Ge system and compared to the same total charge summed up over the clean vacuum/semiconductor Ge(100)  $\times$ (2  $\times$  1) slab with bottom passivating H atoms. This total charge transfer analysis indicates that the 700 K annealed interface depletes the Ge substrate by 9.23 |*e*| of charge corresponding to a normalized charge transfer of  $-6.88 \times 10^{-2}$  |*e*|/Å<sup>2</sup> (Fig. 6). The 1100 K annealed *a*-Al<sub>2</sub>O<sub>3</sub>/Ge interface depletes the Ge substrate of 9.12 |*e*| resulting in -6.80



FIG. 8. (Color) (a) a-Al<sub>2</sub>O<sub>3</sub> and (b) a-ZrO<sub>2</sub> surfaces after annealing, cooling, and relaxation. Al: dark blue, Zr: light blue, O: red. Note the surfaces are capped by oxygen atoms.

 $\times 10^{-2} |e|/Å^2$  of normalized charge transfer (Fig. 6). This large interfacial dipole would have a negative effect on the a-Al<sub>2</sub>O<sub>3</sub>/Ge interface performance in microelectronics applications.

The Bader charge analysis of the vacuum/a-Al<sub>2</sub>O<sub>3</sub> slab indicates a mild charge rearrangement after surface formation with an average surface O atom depletion of ~0.05 |e|



FIG. 9. (Color) (a) a-Al<sub>2</sub>O<sub>3</sub>/Ge and (b) a-ZrO<sub>2</sub>/Ge interfaces during the high-temperature annealing stage (1100 K). Al: dark blue, Zr: light blue, O: red. Note that the interface is different in types of bonds and substrate distortion.

in comparison with the slab in-bulk oxygens [Fig. 8(a)]. However, since the slab thickness is only ~7.5 Å, this surface depletion may differ for thicker slabs.

The DFT annealing of the vacuum/*a*-ZrO<sub>2</sub> slab with two vacuum interfaces reveals trends similar to the vacuum/*a*-Al<sub>2</sub>O<sub>3</sub> slab dynamics (Fig. 8). The oxygen atoms migrate to the surface creating O-rich surface capping, while Zr atoms migrate into the bulk. In the *a*-ZrO<sub>2</sub> bulk, Zr predominantly has six or seven nearest neighbors (Fig. 2). The Zr atom located at the oxide-vacuum interface would likely have a lower number of nearest neighbors thereby increasing the total energy of the system. The bulk O atoms predominantly have only three or four nearest neighbors in the *a*-ZrO<sub>2</sub> bulk (Fig. 2) and will more likely accommodate the vacuum/oxide interface geometry without significantly increasing the total energy of the system.

The a-ZrO<sub>2</sub>/Ge interfacial bonding is different from the vacuum/a-ZrO2 interfacial bonding. Whereas the oxide/ interface demonstrates O-enrichment, vacuum the a-ZrO<sub>2</sub>/Ge interfaces annealed at 700 K and 1100 K have roughly equal numbers of Zr-O-Ge and O-Zr-Ge bonds in the interface region (Fig. 7). During annealing (700 or 1100 K), [Fig. 9(b)], the interface has approximately 1.5 times more long Zr–Ge bonds (empirical length  $\sim 3$  Å) than short O–Ge bonds (empirical length  $\sim 2$  Å) with oxygen atoms tending to bridge between Zr atoms [Fig. 9(b)]. However, during the final relaxation, the interface is compacted; the average interatomic distance decreases and more short O-Ge bonds are formed roughly balancing the number of long Zr-Ge bonds. Increasing the annealing temperature from 700 to 1100 K has no significant effect on interface bond populations (Fig. 7). The high number of Zr-Ge bonds will likely create states in the bandgap that will pin the Fermi level. The electronic structure of a-ZrO<sub>2</sub> bonded to an a-GeO<sub>2</sub> passivation layer on Ge have been calculated and indicated significant improvement of the stack electronic structure.42

The fact that the a-ZrO<sub>2</sub>/Ge interface has bidirectional bonding in contrast to the unidirectional bonding of the a-Al<sub>2</sub>O<sub>3</sub>/Ge interface has a significant effect on the interface polarity. The terms "unidirectional" and "bidirectional" are employed to differentiate between interface in which all the bond dipoles point in the same direction versus one in which bond dipoles point in opposite directions.

The Bader charge analysis of a-ZrO<sub>2</sub>/Ge interfaces annealed at two different temperatures indicates that Ge atoms bonded to O lose about ~0.3–0.9 |*e*| of atomic charge, while Ge atoms bonded to Zr gain about ~0.2–0.7 |*e*|. The total charge depletion in the Ge substrate is estimated to be ~0.40 |*e*| or  $-2.98 \times 10^{-3} |e|/Å^2$  for the 700 K annealed interface (Fig. 7), and ~0.34 |*e*| or  $-2.53 \times 10^{-3} |e|/Å^2$  for the 1100 K annealed one (Fig. 7). Therefore, the total charge transfer through the interface is about ~23–27 times smaller for a-ZrO<sub>2</sub>/Ge compared to a-Al<sub>2</sub>O<sub>3</sub>/Ge consistent with the fact that the a-ZrO<sub>2</sub>/Ge interface with O–Zr–Ge and Zr–O–Ge bonds has compensating bond dipoles, while the a-Al<sub>2</sub>O<sub>3</sub>/Ge interface has only unidirectional Al–O–Ge bond dipoles.

indicates a mild charge depletion of the vacuum/oxide surface O atoms on average by  $\sim 0.09 |e|$  in comparison with the bulk oxygens in the slab [Fig. 8(b)].

## B. Coordination changes induced by bonding at the oxide/semiconductor and vacuum/oxide interfaces

The interfacial coordination number distribution has a direct impact on electronic properties and microelectronics device performance. To understand how the oxide structure is altered by bonding to Ge, the change in surface coordination after bonding to Ge can be compared for the a-Al<sub>2</sub>O<sub>3</sub>/Ge and a-ZrO<sub>2</sub>/Ge interfaces. Note that in computer simulations the "coordination" value is determined by the number of nearest neighbors within a certain cutoff radius; this can result in small differences in coordination number distributions. Below the coordination numbers of the surface atoms at the vacuum/oxide and oxide/semiconductor perturbs the coordination numbers of the surface oxide atoms.

The *a*-Al<sub>2</sub>O<sub>3</sub> vacuum/oxide interface with surface oxygen enrichment has a roughly equal partition of two- and three-coordinated surface oxygen atoms, while the Al atoms closest to the surface and forming bonds to surface O atoms have ~15% of three-fold, ~75% of four-fold and ~10% of five-fold coordinated atoms [Fig. 8(a)]. The Ge(100)(2×1) vacuum/semiconductor surface dimer atoms have a coordination of 3.

The stacking of a-Al<sub>2</sub>O<sub>3</sub> on Ge(100)(2×1) reconstruction perturbs the Ge substrate coordination distribution but has no significant effect on the O interface coordination distribution both for the 700 and 1100 K annealed cases. For the 700 K a-Al<sub>2</sub>O<sub>3</sub>/Ge annealed interface (Fig. 6), Ge atoms switch from 100% three-fold coordination at the vacuum interface to 45% three- and four-fold coordination and 10% two-fold coordination. The two-fold coordinated Ge atoms are those which are pulled out of the substrate and are bonded only to O atoms. Some of Ge dimer atoms do not form bonds to the oxide, thereby preserving three-fold coordination. The high-temperature annealed interface (1100 K, Fig. 6) has only minor deviations in the interfacial Ge coordination distribution in comparison with the low-temperature annealed case (700 K, Fig. 6) having an equal partition of three- and four-coordinated Ge atoms with no two folded ones; the absence of two fold coordinated Ge atoms at high temperature compared to low temperature is probably just due to the limited sample size. The oxygen atoms in the a-Al<sub>2</sub>O<sub>3</sub>/Ge interface region for both annealing temperatures have nearly identical total coordination numbers (i.e., O-Al plus O–Ge) as the oxygen at the vacuum/oxide a-Al<sub>2</sub>O<sub>3</sub> surface: roughly equal partition of two- and three-coordinated oxygens. A few O atoms diffuse into subsurface Ge to form two bonds to Ge atoms thereby breaking Ge-Ge bonds. Since the Al atoms do not make bonds to the Ge substrate, the Al atoms in a-Al<sub>2</sub>O<sub>3</sub> closest to the Ge interface retain the coordination distribution of subsurface Al atoms at the a-Al<sub>2</sub>O<sub>3</sub>/vacuum interface.

The Bader charge analysis of the a-ZrO<sub>2</sub> slab in vacuum

The vacuum/oxide *a*-ZrO<sub>2</sub> surface has an approximately





FIG. 10. (Color online) Average Ge deviation per layer after interface formation. Layers 1–3 are fixed layers of Ge substrate. Layers 8–9 are surface dimer layers of the  $Ge(100)(2 \times 1)$  surface reconstruction.

equal partition of two- and threefold coordinated O atoms, the same as the a-Al<sub>2</sub>O<sub>3</sub> slab. The subsurface Zr atoms bonded to the surface oxygens exhibit  $\sim 37\%$  five-coordinate and  $\sim 63\%$  six-coordinate partitions [Fig. 8(b)]. In contrast, the a-ZrO<sub>2</sub>/Ge interface has a roughly equal partition of two- and three-coordinated O (Fig. 7), demonstrating that stacking to the Ge substrate does not effect the interfacial O coordination distribution. However, the Ge coordination distribution is altered by the stacking from threefold to an equal partition of three- and fourfold for the surface atoms similar to a-Al<sub>2</sub>O<sub>3</sub>/Ge. There are no twofold coordinated Ge atoms for the 700 and 1100 K annealed a-ZrO<sub>2</sub>/Ge interfaces. The interface Zr atoms forming bonds to Ge have a wide coordination distribution between 4 and 7 (note this includes Zr-O and Zr-Ge bonds); this is broader than the Zr coordination distribution at the a-ZrO<sub>2</sub>/vacuum interface. Increasing the annealing temperature from 700 to 1100 K does not significantly affect the a-ZrO<sub>2</sub>/Ge interface coordination.

## C. Interfacial roughness induced by bonding at the oxide/semiconductor interface

The interface roughness with large intermixing can have a deleterious impact on carrier mobility and total device performance. The DFT simulations demonstrated higher Ge substrate deformation and higher intermixing for a-Al<sub>2</sub>O<sub>3</sub>/Ge interfaces in comparison with a-ZrO<sub>2</sub>/Ge (Figs. 6 and 7). To quantify Ge substrate deformation, the average Ge positional deviation per horizontal layer with respect to the relaxed clean  $Ge(100)(2 \times 1)$  slab was calculated using the following norm:  $\Delta R_i = (1/N_i) \Sigma_j |R_j - R_{0j}|$ , where  $N_i$  is the number of Ge atoms in horizontal layer *i*,  $\overline{R}_i$  and  $\overline{R}_{0i}$  are coordinates of Ge atom j belonging to the horizontal layer iafter the interface relaxation and in the initial relaxed clean  $Ge(100)(2 \times 1)$  slab, while index *j* goes along every Ge atom in horizontal layer *i*. The Ge(100)( $2 \times 1$ ) slab has eight atoms per layer. The average Ge deviation per layer is presented in Fig. 10. The first three layers have zero deviation since they are fixed in their bulk positions.

The quantified deformation data presented in Fig. 10 are consistent with greater Ge substrate deformation at the a-Al<sub>2</sub>O<sub>3</sub>/Ge interface than at the a-ZrO<sub>2</sub>/Ge interface. For the 700 K annealed a-Al<sub>2</sub>O<sub>3</sub>/Ge interface, the surface dimer atoms (layers 8 and 9) deviate on average by 1.3 and 2.5 Å, respectively, while the same Ge dimer atoms in the a-ZrO<sub>2</sub>/Ge interface deviate on average by only 1.0 and 0.9 Å (Fig. 10). The same general trend is maintained for the other subsurface layers (Fig. 10). Some of Ge dimer atoms are pulled up by the a-Al<sub>2</sub>O, thereby distorting the Ge surface and creating vacancies that facilitate O diffusion.

Increasing the annealing temperature to 1100 K preserves the larger deformation in the a-Al<sub>2</sub>O<sub>3</sub>/Ge interface versus a-ZrO<sub>2</sub>/Ge with dimer atom deviations of 1.7 Å, 1.5 Å (a-Al<sub>2</sub>O<sub>3</sub>/Ge) versus 0.7 Å, 1.2 Å (a-ZrO<sub>2</sub>/Ge). For a-ZrO<sub>2</sub>/Ge, increasing the annealing temperature from 700 to 1100 K leaves the Ge substrate deformation unchanged (Fig. 7). Conversely, for a-Al<sub>2</sub>O<sub>3</sub>/Ge interfaces, increasing the annealing temperature from 700 to 1100 K creates substantially greater Ge substrate deformation (Fig. 6). In addition, annealing at higher temperature (1100 K) leads to microcavity formation in a-Al<sub>2</sub>O<sub>3</sub> oxide (Fig. 6).

Analysis of the a-ZrO<sub>2</sub>/Ge interface evolution indicates substantial deformation of the Ge substrate during annealing at 1100 K (Fig. 7). However, subsequent final relaxation leads to significant recovery of the Ge substrate regular lattice structure. This is mainly due to the absence of atomic diffusion from oxide into the substrate in a-ZrO<sub>2</sub>/Ge system, which otherwise would create lattice deformation centers. Although for both a-Al<sub>2</sub>O<sub>3</sub>/Ge and a-ZrO<sub>2</sub>/Ge interfaces DFT MD annealing was started with bulk oxide samples in contact with Ge substrate, the final outcome of the simulations revealed substantial differences in interface bonding and deformation.

# D. Mechanical and thermochemical properties of a-Al<sub>2</sub>O<sub>3</sub> versus a-ZrO<sub>2</sub> responsible for differences in semiconductor bonding

### 1. Mechanical property differences

The smaller substrate deformation at the a-ZrO<sub>2</sub>/Ge interface compared to the a-Al<sub>2</sub>O<sub>3</sub>/Ge interface is consistent with relative bulk moduli and the ADFs. The calculated ADF for bulk a-Al<sub>2</sub>O<sub>3</sub> and a-ZrO<sub>2</sub> samples have a standard deviation of 23.7° for O-Al-O angles, while O-Zr-O angles have a standard deviation of 28.7° indicating a larger flexibility of bond angles in a-ZrO<sub>2</sub>, consistent with less deformation and intermixing in a-ZrO<sub>2</sub>/Ge interfaces in comparison with a-Al<sub>2</sub>O<sub>3</sub>/Ge ones (Figs. 6 and 7). The a-ZrO<sub>2</sub> has a lower DFT-calculated bulk modulus (B=77.9 GPa) than a-Al<sub>2</sub>O<sub>3</sub> (B=96.9 GPa) [a-Al<sub>2</sub>O<sub>3</sub> experimental value -89.3 GPa (Ref. 43)] but both are larger than the DFT calculated bulk modulus of crystalline Ge (57.8 GPa). The difference between the DFT calculated crystalline Ge and a-ZrO<sub>2</sub> bulk moduli is 35% compared to the difference between Ge and a-Al<sub>2</sub>O<sub>3</sub> of 68% again consistent with smaller deformation of Ge at the a-ZrO<sub>2</sub>/Ge interface compared to the a-Al<sub>2</sub>O<sub>3</sub>/Ge interface.

### 2. Thermochemical property differences

The possible interfacial solid state reactions were estimated from the Gibbs free energy change in O transfer from the oxide to the substrate to form GeO<sub>2</sub> or GeO oxides. Creation of GeO<sub>2</sub> oxide was found to be endothermic and required 537.1 and 520.6 kJ/mol (normalized to one GeO<sub>2</sub>) unit) for a-Al<sub>2</sub>O<sub>3</sub>/Ge and a-ZrO<sub>2</sub>/Ge interfaces, respectively. Creation of GeO interfacial oxides is also endothermic, requiring 296.7 and 288.4 kJ/mol (normalized to one GeO unit) for a-Al<sub>2</sub>O<sub>3</sub>/Ge and a-ZrO<sub>2</sub>/Ge interfaces, respectively.<sup>36</sup> The temperature-dependent term is not significant enough to cause reaction exothermicity at reasonable processing temperatures. Note that interfaces often are not stoichiometric, which can significantly affect Gibbs energy change for interfacial reactions in oxygen-rich conditions. Therefore, the presented values can be considered only as estimates for interfacial oxide  $\text{GeO}_x$  ( $1 \le x \le 2$ ) formation. The fact that O transfer reaction enthalpies from a-Al<sub>2</sub>O<sub>3</sub> and a-ZrO<sub>2</sub> to Ge to form GeO or GeO<sub>2</sub> are endothermic and close in value for a-Al<sub>2</sub>O<sub>3</sub> and a-ZrO<sub>2</sub> indicates that intermixing at the a-Al<sub>2</sub>O<sub>3</sub>/Ge interface should be attributed mainly to dynamic rather than thermodynamic phenomena.

### 3. Kinetic property differences

MD simulations reveal that subsurface diffusion of O atoms can be one of the causes of interface deformation and intermixing. Oxygen diffusing into Ge creates centers of Ge lattice deformation. The bulk thermodynamics of oxygen diffusion into Ge is very similar for a-Al<sub>2</sub>O<sub>3</sub>/Ge and a-ZrO<sub>2</sub>/Ge interfaces; however, the kinetics and surface thermodynamics are quite different. When the oxide pulls Ge atoms up, vacancies are created for O diffusion (Fig. 6) because gross distortion of the Ge lattice creates partially filled Ge dangling bonds that effectively lower the activation barrier for oxygen diffusion. Since a-Al<sub>2</sub>O<sub>3</sub> more readily distorts the Ge lattice than a-ZrO<sub>2</sub>, the former creates more oxygen diffusion despite any difference in bulk oxygen diffusion thermodynamics.

### E. Discussion of possible statistical errors

To double check that the DFT-MD interface kinetic difference between a-Al<sub>2</sub>O<sub>3</sub>/Ge and a-ZrO<sub>2</sub>/Ge are not just due to random differences between a small number of DFT-MD runs, it is informative to estimate average maximal oxide atom shift in interface region during DFT MD runs. The shift was estimated along the X-Y plane parallel to the interface. The statistics were obtained from an  $\sim$ 2.5 Å thick oxide layer contacting semiconductor substrate containing  $\sim$ 20–25 "oxide interface" atoms. For 700 K annealed a-Al<sub>2</sub>O<sub>3</sub>/Ge interfaces, an average maximal shift of interface oxide atoms was ~2.7 Å, while for 1100 K annealed a-Al<sub>2</sub>O<sub>3</sub>/Ge interface it was ~4.0 Å. The same analysis for 700 K annealed a-ZrO<sub>2</sub>/Ge interface indicated average maximal shift of  $\sim 1.6$  Å, while for 1100 K annealed a-ZrO<sub>2</sub>/Ge interface it was ~2.6 Å. These results are consistent with faster kinetics for higher temperature annealing cases and with larger deformation in a-Al<sub>2</sub>O<sub>3</sub>/Ge interfaces in comparison with a-ZrO<sub>2</sub>/Ge ones. These average maximal shift statistics compared to DFT Ge–Ge bondlength of  $\sim 2.5$  Å demonstrate that during DFT MD runs, oxide interfacial atoms very effectively sample Ge(100)(2×1) 2D surface pattern. This effective sampling of Ge(100)(2×1) surface pattern indicates, that initial atomic arrangement has limited effect on final atomic configuration of investigated interfaces. The average maximal shift during annealing rapidly increases approximately for the first 500–600 fs, then stabilizes; finally in the last  $\sim 200$  fs it looks nearly constant. The stabilization of the atomic position after 600–800 fs indicates that the time scale is enough to stabilize the oxide at the interface.

DFT MD is a very accurate simulation technique, which requires significant computational resources and time. Although better statistics can be obtained by performing many simulations with different samples and initial configurations, the very high cost of DFT MD runs make this impractical within reasonable time at modern computational facilities. The generation of another realistic classical sample and its subsequent DFT annealing would provide a sample with different atomic arrangements, but very similar averaged bulk properties such as RDFs, coordination distributions, and average coordination numbers because only these samples would pass realism test by comparison to the reference sample. The initial interface atomic arrangement has wider variation from system to system. However investigation of amorphous/crystalline interface makes the initial configuration more robust and general since amorphous surface with its high level of randomization inherently provides enhanced level of generality by sampling much more possibilities of initial interatomic bonding in configuration space of oxide/ semiconductor interface. Performing DFT MD at finite temperature adds a whole new dimension of realism by probing different interface bonding configurations over time effectively sampling  $Ge(100)(2 \times 1)$  two-dimensional (2D) surface pattern. The fact that our results demonstrate good correlation to experimental data and interface annealing at the elevated (1100 K) temperature leads to the same qualitative results as interface annealing at 700 K support generality and reliability of the presented a-Al<sub>2</sub>O<sub>3</sub>/Ge and a-ZrO<sub>2</sub>/Ge interface evolution simulations.

### F. Discussion of simulation methods

There are several simulation approaches which potentially can be considered for modeling of amorphous oxidesemiconductor interfaces:

- (a) Kinetic Monte Carlo (KMC) simulations.<sup>44–46</sup> KMC simulations can simulate the time evolution of certain processes occurring with a given rate. However, these rates are input variables for KMC simulations and are often obtained from DFT simulations of the energy barriers for certain set of system transitions.
- (b) DFT MD simulations with oxide atoms randomly bombarding the semiconductor surface trying to simulate atom-by-atom deposition. However, nearly all oxides including Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub>, evaporate incongruently so this is just a approximate model for molecular beam deposition grown oxide/semiconductor interfaces.

(c) DFT MD simulations with previously prepared bulk amorphous sample stacked to the semiconductor surface and relaxed or annealed-cooled-relaxed as it was presented in this paper.

Each of these methods has its own advantages and disadvantages, which should meet certain strict criteria of applicability. One of the major criteria is realism, computational efficiency, and achievable simulated time scale.

KMC simulations are relatively computationally efficient, provide long time scale modeling and could simulate atom-by-atom deposition. However for atomistic modeling of oxide-semiconductor interface evolution, KMC would provide lower accuracy than DFT MD, since KMC simulations replace the true atomic dynamics with statistically equivalent kinetics. The KMC simulations are based on a set of energy barrier calculations and associated rates for various configurations and transitions between the configurations. The DFT MD simulations presented in this paper indicated significant deformation in the substrate, interface, and oxide regions with a very large number of degrees of freedom. An attempt to reproduce a realism of such DFT MD simulations with 3D KMC would require taking into account an unrealistic number of atomic configurations, transition barriers between them and DFT-calculated activation energies.

Method B, DFT-MD simulations with oxide atoms randomly bombarding the semiconductor surface cannot accurately model experimental oxide-semiconductor interface growth for three reasons. (a) With the exception of  $LaAl_2O_3$ , nearly all gate oxide evaporate incongruently so to form stoichiometric films using molecular beam deposition, a second oxygen source must be employed or postdeposition annealing must be employed. (b) Quantitative analysis of the time scale needed to deposit 100 atoms of oxide at realistic experimental deposition rate shows that it would require many orders of magnitude longer time scale than picoseconds, which modern DFT MD can simulate. The fastest MBE deposition rate is  $\sim 0.1 \text{ ML/s}$ ,<sup>47</sup> the fastest metal organic chemical vapor deposition (MOCVD) is  $\sim 3$  ML/s (Ref. 48) and the fastest sputtering deposition is  $\sim 1 \text{ ML/s.}^{49}$  (c) Most gate oxides are deposited by atomic layer deposition, not molecular beam deposition.

Although methods (a) and (b) are able to simulate atomby-atom deposition they raise significant concerns about amorphous film realism. Method (c) described in this paper provides elaborate system of checks to verify high quality of the utilized amorphous sample. Based on such considerations, it is reasonable to conclude that the method (c) which stacks bulk oxide on the semiconductor substrate with subsequent relaxation or annealing-cooling-relaxation (as presented in this paper) provides the most realistic computational approach affordable for modern computational facilities. Although it has some disadvantages, it has been successfully used by many groups for atomistic simulations of oxide-semiconductor interfaces. Tse and Robertson successfully utilized this approach for modeling of ZrO<sub>2</sub>/Ge.<sup>4</sup> Peacock et al.,<sup>50,51</sup> Puthenkovilakam et al.,<sup>52,53</sup> Fonseca et al.,<sup>54</sup> and Dong et al.<sup>55</sup> successfully applied it to simulations of ZrO<sub>2</sub>/Si, ZrSiO<sub>4</sub>/Si and HfO<sub>2</sub>/Si interfaces. Zhang et al.,<sup>8</sup>

Peacock and Robertson,<sup>56</sup> and Forst *et al.*,<sup>57</sup> and Robertson and Peacock<sup>58</sup> used it for modeling of SrTiO<sub>3</sub>/Si interface. Broqvist and co-workers used it for simulations of a-HfO<sub>2</sub>/a-SiO<sub>2</sub>/Si and HfO<sub>2</sub>/SiO<sub>2</sub> stacks.<sup>10,34,59</sup>

# G. Comparison to experimental a-Al<sub>2</sub>O<sub>3</sub>/Ge and a-ZrO<sub>2</sub>/Ge interfaces responsible for differences in semiconductor bonding

The DFT-MD simulations make several predictions which can be compared to experiments. (1) Under ideal deposition conditions, the ZrO<sub>2</sub>/Ge interface should be more abrupt than the a-Al<sub>2</sub>O<sub>3</sub>/Ge interface. (2) For a-ZrO<sub>2</sub>/Ge and a-Al<sub>2</sub>O<sub>3</sub>, the interfacial bonds are polar covalent and both the oxide and substrate atoms should retain nearly bulklike electron binding energy in x-ray photoelectron spectroscopy (XPS). For comparison to experiment, the differences in electron charge associated with atoms at the oxide/ semiconductor interface and in the bulk were calculated by comparing the Bader charges of the oxide/Ge interface atoms with the same atoms in bulk oxide and Ge. For  $a-ZrO_2/Ge$ , the changes in Bader charge are between +0.05 and +0.32|e|for Zr, between -0.06 and +0.03|e| for O, between -0.5|e|and +0.3|e| for Ge; a negative change in Bader charge means an electron charge depletion at a particular atom. Therefore for a-ZrO<sub>2</sub>/Ge, it would be predicted the XPS peaks for the interfacial oxide would be bulk-like and a slight broadening might be observed for interfacial Ge. For  $a-Al_2O_3/Ge$ , the changes in Bader charge are +0.03|e| to +0.2|e| for Al, -0.3|e| to -0.1|e| for O, and -0.8|e| to -0.4|e| for Ge. Therefore, for a-Al<sub>2</sub>O<sub>3</sub>/Ge, it would be predicted that the XPS peaks for the interfacial oxide would be bulklike and a very small Ge<sup>+1</sup> component should be observed for interfacial Ge. As a control, we also calculated the Bader charge change in a thin amorphous GeO<sub>2</sub> layer. In a 2 ML GeO<sub>2</sub> layer, the Ge atoms have charges between -1|e| and -2|e| compared to the bulk consistent with formation of mostly of a mixture of  $Ge^{+1}$  and  $Ge^{+2}$ .<sup>42</sup> Formation of the *a*-Al<sub>2</sub>O<sub>3</sub>/Ge interface leads to much greater total charge transfer from Ge to the oxide than formation of the a-ZrO<sub>2</sub>/Ge interface, and the interfacial and bulk oxide atoms in the a-Al<sub>2</sub>O<sub>3</sub>/Ge stack demonstrate very small deviation in Bader charges; this implies that the charge pulled into a-Al<sub>2</sub>O<sub>3</sub> oxide after interface formation is distributed with a high degree of homogeneity within the oxide.

To compare the DFT-MD simulations to experiment, the oxide deposition method must be considered since the oxide deposition method can disrupt the interface. Unlike silicon, annealing of high-k/Ge interfaces need not produce an interlayer oxide formation;<sup>60,61</sup> therefore, interlayer oxide formation is specific to the oxide deposition technique. There three common gate oxide deposition methods are (a) atomic layer deposition (ALD) or MOCVD; (b) sputter deposition; (c) oxidation of a metal film.

Most studies on gate oxide deposition on Ge employ ALD. Nearly all papers show the need to remove the native oxide prior to ALD because the native oxide is highly defective. On both Si and Ge, the ALD process is almost always initiated using one or more pulses of water vapor. These water pulses disrupt the Ge surface, create an oxide with a high hydroxyl content, and/or create an oxide in which the Ge has a large range of valence states. Both hydroxyl content<sup>62</sup> and low valence state  $\text{GeO}_x$  are strongly correlated with a high interfacial trap density.<sup>63</sup> To mitigate this problem, many research groups passivate the surface prior to ALD oxide deposition using either  $NH_3$ ,<sup>64</sup> ozone,<sup>65</sup> or high pressure  $O_2$  (Refs. 66 and 67) to form either a GeO<sub>2</sub> layer or a GeON passivation layer which is only 1 nm thick and contains only Ge<sup>+4</sup> with a low OH content. ALD oxides typically are slightly nonstoichiometric so their insulating properties are improved by postdeposition annealing (PDA). For PDA above 500 °C, germanium monoxide is observed to diffuse into the oxide and accumulate on the surface of the oxide due to the reaction  $\text{GeO}_2$ +Ge $\rightarrow$ 2GeO.<sup>68,69</sup> The effect of a passivation layer on interfacial bonding and electronic structure between an amorphous oxide and Ge(100) will be addressed in a future paper. Due to the thermal instability and low dielectric constant of GeO<sub>2</sub>, it is desirable to directly bond oxide to Ge (Ref. 70) using either sputter or electron beam deposition techniques.

In sputter deposition, an oxide target is bombarded with energetic ions and secondary vaporized oxide particles are directed at the substrate. It is extremely rare for an oxide to evaporate congruently so  $O_2$  is always present in the deposition chamber during oxide sputter deposition; therefore some  $GeO_x$  formation will occur and the lattice will be disrupted. Kamata et al.<sup>61</sup> formed ZrO<sub>2</sub>/Ge and HfO<sub>2</sub>/Ge interfaces by sputter deposition from an oxide target onto etched Ge wafers. TEM showed that the as-deposited wafers had a small interface layer (1 nm of probably  $GeO_x$ ) but annealing to 500 °C completely removed the interface layer for ZrO<sub>2</sub>/Ge and an abrupt smooth interface was formed without distortion in the Ge substrate. The interface layer could have been formed in the sputter deposition process because, as noted above, oxygen is present during sputter deposition even from an oxide target. The absence of an interfacial layer after annealing is consistent with the ZrO<sub>2</sub>/Ge interface being thermodynamically stable as predicted by the DFT-MD simulations.

Electron beam oxide deposition is employed for gate oxide formation on Ge using two methods. (i) An oxide can be directly evaporated by an electron beam. Nearly all oxides evaporate incongruently resulting in  $O_2$  generation; the  $O_2$ can react with Ge disrupting the lattice. (ii) A thin metal such as Hf or Zr is deposited at low temperature on Ge and oxidized using ozone.<sup>71</sup> Since the metal is more reactive to  $O_3$ than Ge and metal oxide are reasonably good diffusion barriers, this can result in the formation of abrupt oxide/Ge interfaces.

Data from three studies are strongly consistent with the DFT-MD simulations: (1) Chui *et al.*<sup>72</sup> using XPS to study the bonding between *a*-ZrO<sub>2</sub>/Ge where ZrO<sub>2</sub> was deposited by uv ozone oxidation of a sputter deposited Zr at 300 K on a HF etched Ge(100) surface. No Ge was detected inside the ZrO<sub>2</sub>. The interfacial GeO<sub>x</sub> layer was only 1.9–3.6 Å thick and was mainly Ge<sup>+1</sup> consistent with formation of a thin amorphous 2 ML GeO<sub>2</sub> layer with the charge distribution predicted above. (2) Chi *et al.*<sup>73</sup> used both transmission electron microscopy (TEM) and angle resolved XPS study the

bonding between a-ZrO<sub>2</sub>/Ge where ZrO<sub>2</sub> was deposited by uv ozone oxidation of a sputter deposited Zr at 50 °C on a de-ionized water-rinsed Ge(100) surface. The Zr films were 10, 20, and 30 Å thick. For the 30 Å films, all the Zr was in the Zr<sup>+4</sup> oxidation state of ZrO<sub>2</sub>, while for Ge, all the atoms were in the Ge<sup>+0</sup> oxidation state of bulk Ge consistent with the DFT-MD calculations. The TEM images of the 30 Å a-ZrO<sub>2</sub>/Ge show an abrupt interface consistent with the DFT-MD calculations. (3) Kamata *et al.*<sup>61</sup> formed ZrO<sub>2</sub>/Ge and HfO<sub>2</sub>/Ge interfaces by sputter deposition from oxide target onto etched Ge wafers. TEM showed that after annealing to 500 °C, there was an abrupt smooth interface. We note that the annealing induced crystallization of the *a*-ZrO<sub>2</sub>. These results are consistent with the absence of intermixing observed in the DFT-MD calculations.

Data from two studies are consistent with the DFT-MD results for  $a-Al_2O_3/Ge(100)$ : (1) Malafsky<sup>74</sup> studied the deposition of Ge on crystalline Al<sub>2</sub>O<sub>3</sub>. The Ge forms crystalline clusters producing an interface similar to the one in the DFT-MD studies. For submonolayer coverages, Ge is observed by XPS in the Ge<sup>+4</sup> oxidation state consistent with bonding selectively to oxygen atoms on the Al<sub>2</sub>O<sub>3</sub> surface consistent with the DFT-MD results on bonding; the anomalously high experimental oxidation state of the Ge is due to these Ge atoms being adatoms on an oxide surface instead of bulk Ge atoms making multiple Ge-Ge bonds. For all coverages, the experimental Al and O peaks are bulk-like consistent with the small shifts in charge calculated with the DFT-MD simulations. For coverages above 2 ML, the experimental XPS spectrum consisted almost entirely of Ge in Ge<sup>+0</sup> consistent the small shifts in charge calculated with the DFT-MD simulations. (2) Bellenger et al.<sup>75</sup> studied the formation of a-Al<sub>2</sub>O<sub>3</sub>/Ge using Al evaporation onto Ge(100) in the presence of atomic oxygen. TEM images show an amorphous oxide with an abrupt interface to Ge without an obvious interlayer. XPS studies show the Al peak is unshifted compared to that from Al<sub>2</sub>O<sub>3</sub> consistent with the charge changes calculated with DFT-MD. The Ge XPS spectrum shows a small amount of Ge<sup>+2</sup>, Ge<sup>+3</sup>, and Ge<sup>+4</sup> consistent with Ge-O bonds over a region of less than 8 Å. This greater intermixing for Al<sub>2</sub>O<sub>3</sub>/Ge compared to ZrO<sub>2</sub>/Ge is consistent with the DFT-MD calculations, but Bellenger et al.<sup>75</sup> simultaneously exposed the surface to Al and O atoms which would tend to place a bit more oxygen at the interface than oxidation of an Al film so the comparison to the DFT-MD a-ZrO<sub>2</sub>/Ge interfaces cited above is slightly biased.

### **VI. SUMMARY AND CONCLUSIONS**

We presented DFT MD simulations of a-Al<sub>2</sub>O<sub>3</sub> and a-ZrO<sub>2</sub> interfaces with vacuum and with a Ge(100)(2×1) substrate at two different annealing temperatures (700 and 1100 K). Realistic amorphous Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub> samples were generated with a hybrid classical-DFT melt and quench approach, thoroughly tested and demonstrated to have good correlation with experimental results and computer simulations.

The simulations of a-Al<sub>2</sub>O<sub>3</sub> and a-ZrO<sub>2</sub> vacuum/oxide surfaces indicated strong surface chemical selectivity with O

atoms migrating to the surface and Al and Zr atoms migrating into the bulk, creating surface oxygen capping. The stacking of a-Al<sub>2</sub>O<sub>3</sub> to the Ge(100)(2×1) substrate preserves this trend creating an O-enriched interface bonded exclusively through Al-O-Ge bonds with no or few O-Al-Ge ones. The stacking of a-ZrO<sub>2</sub> to the Ge substrate and interface annealing revealed different behavior resulting in roughly equal numbers of Zr-O-Ge and O-Zr-Ge bonds. During the high-temperature anneal, the a-ZrO<sub>2</sub>/Ge interface expansion favors longer Zr-Ge bonds with O atoms bridging between Zr ones. However, cooling and final relaxation result in a more compact interface creating more O-Ge bonds which roughly balance the number of Zr-Ge ones. Due to high bond selectivity, a-Al<sub>2</sub>O<sub>3</sub>/Ge interfaces have strong interface polarity and charge transfer from Ge to a-Al<sub>2</sub>O<sub>3</sub> oxide. Conversely, the a-ZrO<sub>2</sub>/Ge interfaces have roughly equal numbers of Zr-O-Ge and O-Zr-Ge bonds and  $\sim$ 23–27 times less charge transfer.

The effect of the interface annealing temperature was investigated by studying two annealing temperatures: 700 and 1100 K. The a-ZrO<sub>2</sub>/Ge interface reveals no significant deformation or intermixing at either annealing temperature. Conversely, the a-Al<sub>2</sub>O<sub>3</sub>/Ge interface shows a higher interface roughness for the higher temperature (1100 K) annealed interface than for the low-temperature (700 K) one.

A comparison of interface deformation indicates a much stronger deformation and intermixing in a-Al<sub>2</sub>O<sub>3</sub>/Ge interfaces than in a-ZrO<sub>2</sub>/Ge ones. This is consistent with the difference in the bulk moduli and ADFs of bulk a-Al<sub>2</sub>O<sub>3</sub> and a-ZrO<sub>2</sub> oxides. The a-Al<sub>2</sub>O<sub>3</sub> has higher bulk modulus than a-ZrO<sub>2</sub> consistent with more rigid bonding in the a-Al<sub>2</sub>O<sub>3</sub> oxide. The a-ZrO<sub>2</sub> oxide has a higher standard deviation of O-Zr-O angles (28.7°) in comparison with O-Al-O angles  $(23.7^{\circ})$  in *a*-Al<sub>2</sub>O<sub>3</sub> oxide, indicating an enhanced flexibility of the a-ZrO<sub>2</sub> atomic structure that leads to less interface deformation. For amorphous oxide-Ge interfaces, it is more favorable to have oxides which are softer than the semiconductor substrates since it will significantly reduce the possibility for substrate deformation. Substrate deformation provides low barrier pathways for the diffusion of oxygen from the oxide into the Ge substrate.

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