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# Role of Surface Orientation on Atomic Layer Deposited Al<sub>2</sub>O<sub>3</sub>/GaAs Interface Structure and Fermi Level Pinning: A Density Functional Theory Study

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# Role of surface orientation on atomic layer deposited Al<sub>2</sub>O<sub>3</sub>/GaAs interface structure and Fermi level pinning: A density functional theory study

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We investigate the initial surface reaction pathways in the atomic layer deposition (ALD) of Al<sub>2</sub>O<sub>3</sub> on GaAs (111)A and (111)B substrates using precursors trimethylaluminum (TMA) and water to ascertain the effect of surface orientation on device performance. We find that the condition of the respective substrates prior to deposition of TMA and water has a major impact on the surface reactions that follow and on the resulting interface structure. The simulations explain the atomistic mechanism of the interfacial self-cleaning effect in ALD that preferentially removes As oxides. The electronic structure of the resulting atomic configurations indicates states throughout the bandgap for the (111)B structure. By contrast, the (111)A structure has no states in the mid-gap region, thus explaining the significant experimental difference in Fermi Level Pinning behavior for corresponding devices. © 2011 American Institute of Physics. [doi:10.1063/1.3624897]

Fermi level pinning (FLP) at III-V/oxide interfaces has been one of the main obstacles in realizing logic devices based on III-V materials.<sup>1</sup> In a recent experiment, Xu *et al.* showed that FLP at GaAs/oxide interfaces depends strongly on the semiconductor interface orientation,<sup>2</sup> in contrast with earlier theoretical models that postulate FLP to be an intrinsic material property.<sup>3–5</sup> The experiment showed that devices fabricated using atomic layer deposition (ALD) of Al<sub>2</sub>O<sub>3</sub> using trimethylaluminum (TMA) and water on GaAs (111)A (Ga-terminated) exhibit four orders of magnitude higher on-current and better Fermi level unpinning than those fabricated on the (100) and (110) substrates. In addition, the devices fabricated on (111)B (As-terminated) substrate showed close to zero ON-current.

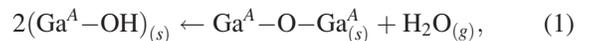
Previous density functional theory (DFT) investigations of the ALD of oxides on III–V materials<sup>6–8</sup> have focused on the atomic and electronic structure of the III–V (100)/ALD-oxide interface. Other models, such as Robertson's model of III–V interface states<sup>5</sup> and Freeouf and Woodall's effective work function model<sup>9</sup> point towards anion-anion bonding as a source of FLP.

Despite its technological importance, the atomic structure of the GaAs (111)A/oxide interface remains poorly understood and the striking difference between its properties and those of (111)B remains unexplained. In this letter, we use *ab initio* DFT to predict the atomic and electronic structure corresponding to the first cycle of ALD deposition of Al<sub>2</sub>O<sub>3</sub> on GaAs (111)A and GaAs (111)B. Given the striking difference in device performance between these two cases,<sup>2</sup> they provide an ideal case to test the predictive power of *ab initio* calculations in this field. We find that the condition of the surfaces pre-deposition has a strong impact on the initial chemical reactions and the resulting interface structures. The reactions and structures thus formed explain the atomistic ori-

gin of the well known preferential removal of As-oxides in ALD.<sup>10,11</sup> We also find that the resulting (111)A interface does not exhibit mid-gap states, in contrast with the (111)B interface, where states exist throughout the band gap.

All our calculations use SeqQUEST, a pseudopotential DFT code that uses contracted Gaussian basis sets.<sup>12</sup> The simulation cells are obtained by replicating a 12-atom unit cell oriented along  $\mathbf{a} = 1/2[110]$ ,  $\mathbf{b} = 1/2[112]$ , and  $\mathbf{c} = [111]$  twice along  $\mathbf{b}$ . We use 2D periodic boundary conditions along  $\mathbf{a}$  and  $\mathbf{b}$  and use  $4 \times 8$  k-points in these directions. This leads to a (111)A and a (111)B surface per simulation cell. We characterize ALD reactions one surface at a time while the other is passivated with pseudo-hydrogen atoms. Additional details of the computational procedure are included in the supplementary material.<sup>13</sup>

Before studying the ALD reactions, we need to determine the initial surface chemistry. We start with both fully hydroxylated (111)A and (111)B surfaces (a common choice as explained in more detail in the supplementary material<sup>13</sup>) and study their stability. In particular, we investigate energetics associated with two surface hydroxides reacting to form a water molecule in the gas phase and leaving an O atom in the surface. The resulting (111)A and (111)B configurations are different with the O bridging between two Ga atoms in (111)A and taking a sub-surface position bonding to both As and Ga in the (111)B (see Fig. 1). Importantly, our DFT calculations show the hydroxylated surface to be energetically favorable for (111)A (by 1.86 eV), Fig. 1(a), but not for (111)B where the oxidized surface and water is 0.95 eV lower in energy, see Fig. 1(b). Thus, the pre-ALD surfaces are different and can be summarized by



where the A and B superscripts denote atoms on the (111)A and (111)B surface, respectively. Inspection of the resulting

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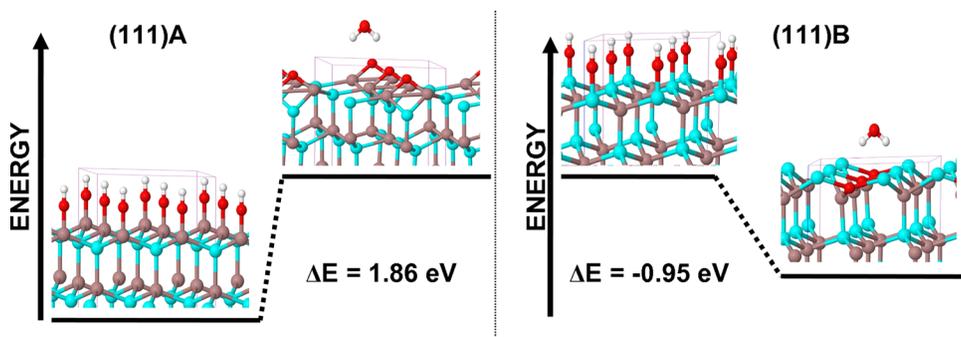
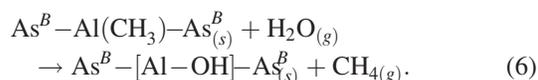
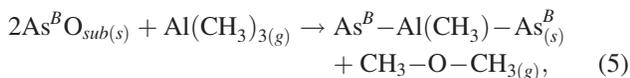
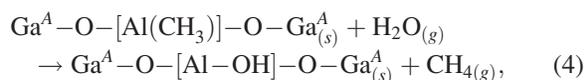
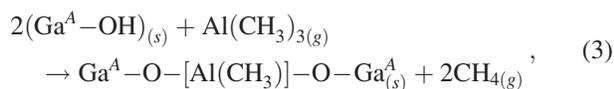


FIG. 1. (Color online) (111)A and B OH terminated surface undergoing transformation indicated by reactions (1)(right) and (2)(left). O, As, Ga, and H atoms are represented by red, larger white, grey, and smaller white spheres, respectively. The box indicates the (2X1) unit cell used in our calculations.

pre-deposition surfaces shows that (111)A would be more hydrophilic than (111)B; this is in agreement with experimental observations<sup>14</sup> providing indirect support to our initial configurations.

Next, we explore possible reactions associated with the first half reaction in the ALD process involving TMA followed by the second half reaction involving water. This is done starting from the lowest energy (111)A and B surfaces obtained in the previous step leading to the following reactions:



Atomistic structures of these two reactions can be found in the supplementary material.<sup>13</sup> The first half reactions proceed very differently on the two surfaces. For the (111)A, a reaction between TMA with a surface OH group releasing a methane molecule and leading to an O-Al bond lowers energy by 1.9 eV and a subsequent reaction with a neighboring OH decreases energy by an additional 1.73 eV. A reaction of the remaining methyl group with water in the second half reaction is also energetically favorable by 0.93 eV. In contrast, on the (111)B surface with the sub-surface oxygen, the oxide is completely removed in a highly exothermic half-reaction (1.83 eV decrease in energy) with TMA releasing dimethyl ether and with Al bonding to two surface As atoms. The half-reaction with water is also highly exothermic (1.11 eV) and it replaces the last methyl group left over from the previous reaction with an OH group. Subsequent half-reactions would proceed in the usual self-terminating fashion, releasing methane at each stage as is expected from the TMA-water ALD process.<sup>15</sup>

As can be seen in Fig. 2, the interface structures obtained at the end of the first ALD cycle for (111)A and (111)B are starkly different. The Ga atoms on the (111)A

interface bond with O atoms which in turn bond with Al atoms. At the (111)B interface, the As atoms bond directly to Al. The surface oxide initially present at the (111)B surface is completely removed in favor of As-Al bonding at the interface, whereas Ga-O bonding persists at the (111)A interface. This preferential cleaning of As-oxides has been termed “interfacial-self cleaning” and is well known in ALD experiments;<sup>11</sup> our simulations provide an atomic mechanism for this process on (111) surfaces. We note that the nature of bonding at the interface is consistent with previous theoretical calculations on the (100) surface,<sup>8,16</sup> where molecular dynamics calculations of Al<sub>2</sub>O<sub>3</sub> slabs on clean, reconstructed (100) III-V surfaces indicate that surface cations are bond with O atoms while surface anions bond with Al atoms. Electronic versions of the atomistic structures thus obtained are available for online simulations and additional exploration on the nanoHUB.<sup>17</sup>

Finally, we investigate the electronic structure of the structures obtained at the end of the half reactions. The Kohn-Sham density of states (DOS) for the two interfaces are compared to bulk GaAs in Fig. 3, with the conduction band edge in bulk set to zero energy. The (111)B structure has a large number of allowed electronic states distributed throughout the band gap, consistent with the experimental observation of significant pinning and zero current obtained for (111)B N metal-oxide-semiconductor field effect transistors (NMOSFETs).<sup>2</sup> By contrast, the (111)A structure only exhibits states very close to the band edges and no additional states in the band gap. This is consistent with the experimental observation of excellent unpinning in the mid-gap region and high on current in (111)A NMOSFETs. Resolving the contribution of individual atoms towards the total DOS shows that the majority of the gap states originate from As and Al atoms at the interface. We observe the presence of

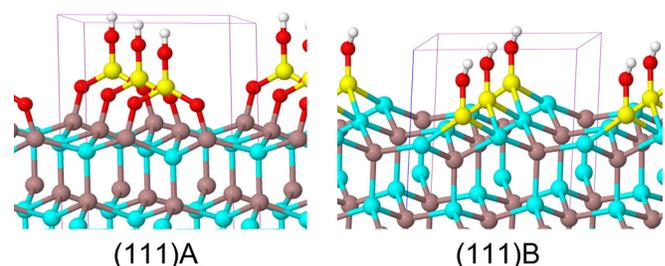


FIG. 2. (Color online) Interface structures obtained at the end of the first cycle of ALD half-reactions on (111)A and B, respectively. Al atoms are represented by yellow spheres.

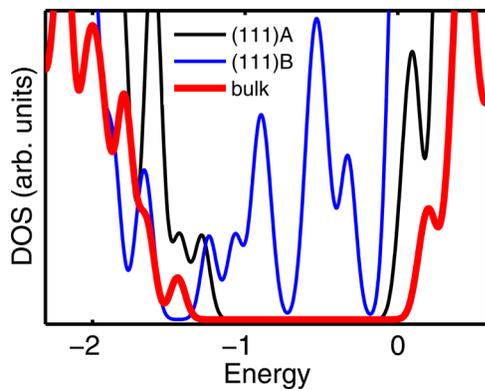


FIG. 3. (Color online) Plot of DOS versus energy for the structures shown in Fig. 2 compared with the DOS of bulk GaAs.

mid-gap states in the absence of As-As bonds at the interface.

In conclusion, our DFT calculations show how the combination of the initial surface chemistry and the preferential removal of As-oxides in the TMA/Water process lead to completely different interface structures with  $\text{Al}_2\text{O}_3$  for the (111)A and B oriented substrates. Furthermore, the electronic structure of the resulting atomic configurations after the first ALD cycle explains the experimental difference in performance of corresponding NMOSFETs. We note that the actual atomic structure at the interfaces may be quite complicated and our study only shows one set of possible initial surface structures and reaction pathways during the ALD process.

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<sup>1</sup>P. Ye, *J. Vac. Sci. Technol. A* **26**, 697 (2008).

<sup>2</sup>M. Xu, K. Xu, R. Contreras, M. Milojevic, T. Shen, O. Koybasi, Y. Wu, R. Wallace, and P. Ye, in *Electron Devices Meeting (IEDM), 2009 IEEE International* (IEEE, New York, 2010), pp. 1–4.

<sup>3</sup>W. Spicer, I. Lindau, P. Skeath, C. Su, and P. Chye, *Phys. Rev. Lett.* **44**, 420 (1980).

<sup>4</sup>H. Hasegawa and H. Ohno, *J. Vac. Sci. Technol. B* **4**, 1130 (1986).

<sup>5</sup>J. Robertson, *Appl. Phys. Lett.* **94**, 152104 (2009).

<sup>6</sup>J. Ren, G. Zhou, Y. Hu, H. Jiang, and D. Zhang, *Appl. Surf. Sci.* **254**, 7115 (2008).

<sup>7</sup>H. Lu, M. Xu, S. Ding, W. Chen, D. Zhang, and L. Wang, *Appl. Phys. Lett.* **89**, 162905 (2006).

<sup>8</sup>E. Chagarov and A. Kummel, *Fundamentals of III-V Semiconductor MOSFETs* (2010), p. 93.

<sup>9</sup>J. Freeouf and J. Woodall, *Appl. Phys. Lett.* **39**, 727 (1981).

<sup>10</sup>M. Huang, Y. Chang, C. Chang, Y. Lee, P. Chang, J. Kwo, T. Wu, and M. Hong, *Appl. Phys. Lett.* **87**, 252104 (2005).

<sup>11</sup>C. Hinkle, A. Sonnet, E. Vogel, S. McDonnell, G. Hughes, M. Milojevic, B. Lee, F. Aguirre-Tostado, K. Choi, H. Kim, J. Kim, and R. Wallace, *Appl. Phys. Lett.* **92**, 071901 (2008).

<sup>12</sup>P. Schultz and R. Muller, SeqQUEST Electronic Structure Code, available at <http://http://dft.sandia.gov/Quest/>.

<sup>13</sup>See supplementary material at <http://dx.doi.org/10.1063/1.3624897> for details of computational procedure and accessing structures on the nanoHUB.

<sup>14</sup>P. D. Ye, private communication.

<sup>15</sup>R. Puurunen, *J. Appl. Phys.* **97**, 121301 (2005).

<sup>16</sup>M. Houssa, E. Chagarov, and A. Kummel, *MRS Bull.* **34**, 504 (2009).

<sup>17</sup>R. P. K. Vedula, G. Bechtol, B. P. Haley, and A. Strachan, *Nanomaterials SeqQUEST DFT*, available at <https://nanohub.org/resources/3982> (2010).