

Title	Decomposition of metal alkylamides, alkyls, and halides at reducible oxide surfaces: mechanism of 'clean-up' during atomic layer deposition of dielectrics onto III-V substrates
Authors	Klejna, Sylwia; Elliott, Simon D.
Publication date	2014-02-21
Original Citation	KLEJNA, S. & ELLIOTT, S. D. 2014. Decomposition of Metal Alkylamides, Alkyls, and Halides at Reducible Oxide Surfaces: Mechanism of 'Clean-up' During Atomic Layer Deposition of Dielectrics onto III-V Substrates. Chemistry of Materials, 26, 2427-2437. <a href="http://dx.doi.org/10.1021/cm403336c">http://dx.doi.org/10.1021/cm403336c</a>
Type of publication	Article (peer-reviewed)
Link to publisher's version	<a href="http://dx.doi.org/10.1021/cm403336c">10.1021/cm403336c</a>
Rights	© 2014 American Chemical Society. This document is the Accepted Manuscript version of a Published Work that appeared in final form in Chemistry of Materials, copyright © American Chemical Society after peer review and technical editing by the publisher. To access the final edited and published work see <a href="http://dx.doi.org/10.1021/cm403336c">http://dx.doi.org/10.1021/cm403336c</a>
Download date	2025-05-20 06:29:47
Item downloaded from	<a href="https://hdl.handle.net/10468/2421">https://hdl.handle.net/10468/2421</a>



# UCC

**University College Cork, Ireland**  
Coláiste na hOllscoile Corcaigh

1 Decomposition of metal alkylamides, alkyls and halides  
2 at reducible oxide surfaces: mechanism of ‘clean-up’  
3 during atomic layer deposition of dielectrics onto III-V  
4 substrates

5 *Sylwia Klejna, Simon D. Elliott\**

6 Tyndall National Institute,

7 University College Cork,

8 Dyke Parade, Cork, Ireland

9

10

11

12

13 **ABSTRACT:** The pairing of high- $k$  dielectric materials with high electron mobility semiconductors for  
14 transistors is facilitated when atomic layer deposition (ALD) is used to deposit the dielectric film. An  
15 interfacial cleaning mechanism ('clean-up') that results in consumption of semiconductor native oxides  
16 and in practically sharp dielectric/semiconductor interfaces has been observed during ALD of  $\text{Al}_2\text{O}_3$ ,  
17  $\text{HfO}_2$ ,  $\text{TiO}_2$  and  $\text{Ta}_2\text{O}_5$  with various degrees of success. We undertake a comprehensive study using  
18 density functional theory (DFT) to explain differences in the performance of various classes of  
19 precursor chemicals in removing native oxide from III-V substrates. The study covers the metals Ta(V),  
20 Ti(IV), Zr(IV), Hf(IV), Al(III), Mg(II) combined with methyl, amide and chloride ligands. Of these, we  
21 show that clean-up is most effective when depositing MgO. Clean-up with metal alkylamides has a  
22 similar mechanism to clean-up with metal methyls insofar as oxygen is scavenged by the metal. The  
23 difference in operation of alkylamide and methyl ligands lies in the affinity of the ligand to the  
24 substrate. Alkylamide is shown to be prone to decomposition rather than the migration of the entire  
25 ligand evinced by methyl. We investigate the multi-step chemical processes associated with  
26 decomposition of alkylamide. These processes can also occur during later cycles of high- $k$  ALD and  
27 give a chemical vapor deposition (CVD) component to the ALD process. These transformations lead to  
28 formation of clean-up products such as aziridine, ethene, N-methyl methyleneimine, hydrogen cyanide  
29 and methane. Some – but not all – of the reactions lead to reduction of surface  $\text{As}_2\text{O}_3$  (*i.e.* clean-up).  
30 These results explain the experimentally-observed accumulation of metallic arsenic and arsenic  
31 suboxide at the interface. Such understanding can help achieve control of oxide-semiconductor  
32 interfaces through the appropriate choice of chemical precursor.

33 **KEYWORDS** atomic layer deposition (ALD), high- $k$  dielectrics, III-V substrate, reducible oxide, clean-  
34 up effect, ALD precursor, metal alkylamide, ligand decomposition, density functional theory (DFT)

35

## 36 1. Introduction

37 The extensive research on pairing of high- $k$  dielectrics materials with high electron mobility  
38 semiconductors has renewed interest in replacing SiO<sub>2</sub>/Si based transistors for future generations of  
39 nanoelectronic devices. The key issue in combining high- $k$  materials for the gate, such as Al<sub>2</sub>O<sub>3</sub> and  
40 HfO<sub>2</sub>, with GaAs or InGaAs III-V semiconductors for the channel is finding a stable passivation of the  
41 interface with acceptably low density of interface states. Several reports suggest that this can be partially  
42 achieved during deposition of the dielectric film using atomic layer deposition (ALD)<sup>1</sup>. The early stages  
43 of ALD growth determine the interface properties and therefore careful optimization of deposition  
44 conditions helps with improving device performance. An interfacial cleaning mechanism that results in  
45 consumption of semiconductor native oxides and in practically sharp dielectric/semiconductor interfaces  
46 has been observed during ALD of Al<sub>2</sub>O<sub>3</sub><sup>2</sup>, HfO<sub>2</sub><sup>3</sup>, TiO<sub>2</sub><sup>4</sup> and Ta<sub>2</sub>O<sub>5</sub><sup>5</sup> on GaAs and InGaAs. This has  
47 been called ‘clean-up’ or ‘self-cleaning’. Although removing native oxides is not sufficient to solve the  
48 Fermi-level pinning problem in devices<sup>6</sup>, it is an important step in the preparation of abrupt interfaces.  
49 The electrical characteristic of the device is improved though when appropriate and optimised  
50 passivation and ALD processing is enabled as suggested in<sup>7</sup>.

51 While the phenomenon of native oxide thinning during semiconductor exposure to ALD metal  
52 precursors has been confirmed in several experiments, the chemistry of this process is not well  
53 understood. First reports on the clean-up effect documented an effective passivation of GaAs-based  
54 substrates with trimethylaluminium (TMA or AlMe<sub>3</sub>; where Me = CH<sub>3</sub>) when depositing Al<sub>2</sub>O<sub>3</sub><sup>8</sup>. For  
55 HfO<sub>2</sub> ALD, the clean-up effect was observed mainly when using hafnium alkylamides, with similar  
56 behaviour shown by tetrakis(ethylmethyldamido)hafnium (TEMAH or Hf(NEtMe)<sub>4</sub>; where Et = C<sub>2</sub>H<sub>5</sub>) or  
57 tetrakis(dimethylamido)hafnium (TDMAH, Hf(NMe<sub>2</sub>)<sub>4</sub>)<sup>3a, 8-9</sup>. A recent study shows that ALD processes  
58 utilizing alkylamide precursors featuring Ti (tetrakis(dimethylamido)titanium, TDMAT, Ti(NMe<sub>2</sub>)<sub>4</sub>) or  
59 Ta (pentakis(dimethylamido)tantalum, PDMAT, Ta(NMe<sub>2</sub>)<sub>5</sub>) also result in the same interfacial cleaning  
60 effect while depositing TiO<sub>2</sub> or Ta<sub>2</sub>O<sub>5</sub> respectively<sup>4b, 5</sup>. These observations indicate that the common

61 requirement for self-cleaning is the use of organometallic or metalorganic precursors. However, the  
62 examples of the purely inorganic HfCl<sub>4</sub> and TiCl<sub>4</sub> ALD processes contradict this assumption. ‘Clean-up’  
63 is also observed with the use of these precursors by Delabie *et al.*<sup>3b</sup> and Granados-Alpizar and Muscat  
64<sup>4a</sup> but was not reported by Frank *et al.*<sup>10</sup>.

65 Common experimental observations are found for interfacial cleaning with TMA and alkylamide  
66 precursors. Generally arsenic oxides are easier to remove than gallium oxides. Higher oxidation states of  
67 both As (As<sup>5+</sup>) and Ga (Ga<sup>3+</sup>) are more sensitive to reduction. Accumulation of metallic arsenic –  
68 arsenic suboxide at the interface has been observed for TMA based ALD<sup>6a</sup> and alkylamide based ALD  
69<sup>9</sup>. It seems that elevating the temperature of the process significantly enhances the clean-up abilities of  
70 alkylamides, and this differentiates these processes from TMA-based clean-up<sup>5, 11</sup>. Granados-Alpizar  
71 and Muscat show differences in surface reactions during GaAs exposure to TMA and TiCl<sub>4</sub> pulses<sup>4a</sup>:  
72 both precursors remove the native oxide layer, but the mechanisms underlying this process seem to be  
73 fundamentally different. TMA deposits an Al<sub>2</sub>O<sub>3</sub> layer and removes a portion of As from the surface,  
74 whereas TiCl<sub>4</sub> removes O and leaves the surface passivated with Cl atoms. The mechanism for  
75 removing oxides with the use of HfCl<sub>4</sub> differs also from the one for TiCl<sub>4</sub>. The growth of hafnium oxide  
76 is enhanced<sup>3b</sup> and growth of titanium oxide is inhibited<sup>4a</sup>. These extensive and sometimes conflicting  
77 studies on interfacial self-cleaning show how little is understood about the chemistry occurring in the  
78 initial cycles of deposition of dielectrics.

79 In this study with the use of DFT we try to provide improved understanding of the chemical principles  
80 underlying ‘clean-up’ and thus rationalize experimental observations. There are not many studies  
81 available on mechanisms during early stages of growth on III-V semiconductors. Typical mechanisms  
82 occurring during ALD on other semiconductors (Si, Ge) are described in numerous publications, as  
83 reviewed by Elliott<sup>12</sup>. Previous atomic-scale simulations of clean-up mechanisms focused on the  
84 interaction of TMA with GaAs<sup>13</sup> and III-V native oxides<sup>14</sup>. TMA was shown to be able to reduce  
85 arsenic oxides into gaseous As<sub>4</sub> and solid GaAs, with Al<sub>2</sub>O<sub>3</sub> formation and C lost as C<sub>2</sub>H<sub>6</sub><sup>14</sup>. DFT

86 revealed that the mechanistic step of reduction takes place when the CH<sub>3</sub> ligand migrates from surface-  
87 bound Al/As/Ga to O and gets oxidised, simultaneously reducing the III-V native oxide substrate. From  
88 the TMA example two interesting conclusions emerge: ligand exchange as well as ligand redox  
89 mechanisms are at play during clean-up and the precursor metal cation provides an energetic sink when  
90 it bonds to oxygen.

91 In the current investigation, building on the example of TMA, we look for an explanation of differences  
92 observed in the operation of different families of metal precursors: alkylamides, methyls and chlorides.  
93 We focus mainly on the clean-up of the arsenic (III) oxide component of the surface utilizing the  
94 Hf[N(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub> precursor during HfO<sub>2</sub> ALD. The choice of the surface model has been previously  
95 motivated and its structure and limitations have been described in detail <sup>14</sup>. The main emphasis here is  
96 on the interaction of the dimethylamido ligand (dma) with the oxide surface with a view to finding  
97 potential redox properties of this ligand. Based on the TMA findings, the metal cation is assumed to be  
98 redox inactive, and to combine with oxide anions to form a dielectric oxide. We postulate that formation  
99 of the dielectric oxide is the driving force for the clean-up effect and confront this by investigating the  
100 clean-up ability of precursors that are chemically different to TMA. Assuming these postulates allows  
101 us to define and separate the factors governing the clean-up effect. In this way, a set of general reactions  
102 is generated and a comparison can be made between a number of different precursors. In the end, this  
103 approach should help with assessing whether clean-up is a general effect, regardless of precursor being  
104 used.

## 105 **2. Computational method & approach**

106 Periodic density functional theory (DFT) at 0 K as implemented in the VASP package <sup>15</sup> was applied as  
107 a reliable method for computation of the ground state electronic structure and total energy of crystalline  
108 materials. We use the generalized gradient approximation (GGA) of Perdew and Wang (PW91) <sup>16</sup> for  
109 the exchange-correlation energy. The core electrons were described with ultrasoft pseudopotentials

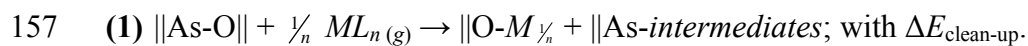
110 (USPP)<sup>17</sup> projected into real space and valence electrons were described with a plane-wave basis with a  
111 kinetic energy cutoff of 396 eV. Geometry optimization was carried out with a sparse Monkhorst-Pack  
112  $k$ -point sampling of reciprocal space. A conjugate-gradient algorithm was used for ionic relaxation with  
113 all ions relaxed until the forces on the ions were less than 0.02 eV/Å.

114 High accuracy was used for bulk oxide calculations: convergence of energies to  $10^{-4}$  eV with respect  
115 to coordinates of ions and cells, 130% of the standard plane-wave cutoff energy, convergence with  
116 respect to  $k$ -point sampling. The total energy versus volume for all models of the bulk oxide structures  
117 was optimized resulting in equilibrium lattice parameters that agreed well with experiment (with  
118 deviation less than 2%)<sup>18</sup>. Lattice parameters and space groups, along with  $k$ -point sampling for these  
119 calculations are given in the supporting information. We used experimental lattice constants for the bulk  
120 model of *arsenolite* arsenic (III) oxide<sup>19</sup> since its crystalline structure did not allow us to perform cell  
121 shape optimization within DFT as explained in detail before<sup>14</sup>. Ions were fully relaxed within the fixed  
122  $\text{As}_2\text{O}_3$  cell and the structural parameters compared well with the experimental values. The *arsenolite*-  
123  $\text{As}_2\text{O}_3$  (010) surface is modeled by periodic slabs separated by 10 Å of vacuum. We use a  $2\times 2$  surface  
124 expansion that contains 1 layer totaling 8 molecular units of  $\text{As}_4\text{O}_6$  (80 atoms) and a  $2\times 2\times 1$   $k$ -point  
125 mesh for surface calculations. This surface is computed to have a surface energy below 0.02 J/m<sup>2</sup>.  
126 Gaseous species (precursor molecules and gas phase products) were individually relaxed in a simulation  
127 box, cubic or rhombohedral, of dimensions  $15\times 15\times 15$  Å, with six  $k$ -points located at the edges of the  
128 first Brillouin zone. Geometrical parameters for all optimised gaseous molecules can be found in the  
129 supporting information.

130 For investigation of the ligand decomposition surface reactions we use the bare  $\text{As}_2\text{O}_3$  (010) surface. For  
131 redox reactions differences in Bader atomic charges<sup>20</sup>,  $\Delta q$ , are analyzed to determine the chemical state  
132 of intermediates and thus help in predicting a final product. The sign convention used in this paper is  
133 that  $\Delta q < 0$  means loss (oxidation of an atom) and  $\Delta q > 0$  means gain (reduction of an atom) of electron  
134 population on atoms taking part in the considered reaction. To study the stability of surface bound

135 intermediates we performed DFT molecular dynamics in the canonical ensemble at around 300° C for  
 136 0.4 ps. At the end of these simulations all surface intermediates were found to be bonded the same as  
 137 their initial configuration, suggesting that no spontaneous reactions occur and that there are barriers to  
 138 overcome on the potential energy surface for any following chemical transformations. We neglect the  
 139 constant contribution to entropy ( $S$ ) from solid surfaces with adsorbates since  $S^{\text{trans}}$  and  $S^{\text{rot}}$  for surfaces  
 140 are approximately zero and  $S^{\text{vib}}$  is approximately constant during the reaction,  $\Delta S^{\text{vib}} = 0$ . Therefore  $\Delta S =$   
 141 0 for surface reactions and the Gibbs free energy profiles closely resemble the DFT potential energy  
 142 surfaces. Reaction energetics are computed with an estimated accuracy of 0.1 eV. Activation energies  
 143 reported here were computed using the nudged elastic band method (NEB)<sup>21</sup>. We used up to 8 images  
 144 for each reaction pathway. The damped molecular dynamics algorithm for ionic relaxation was found to  
 145 be appropriate for the regarded system. Around 1000 steps were needed to converge forces on atoms to  
 146 below 0.05 eV/Å.

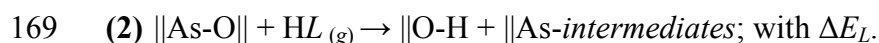
147 In this investigation we consider the process where the adsorbed metal precursor molecules, with the  
 148 general formula  $ML_n$  ( $M = \text{Mg(II)}, \text{Al(III)}, \text{Ti(IV)}, \text{Zr(IV)}, \text{Hf(IV)}, \text{Ta(V)}$ ;  $L = [\text{N(Me)}_2]^-$ ,  $[\text{Me}]^-$ ,  $[\text{Cl}]^-$ ;  $n$   
 149 – oxidation state of metal), undergo a series of clean-up transformations leading to removal of the native  
 150 oxides of III-V substrates. As outlined in section 1, we propose that the main and most  
 151 thermodynamically stable product of these transformations is a film of dielectric metal oxide with the  
 152 general formula  $M_2O_n$ . (Thus, there is no reduction or oxidation of  $M$ ). Another factor in the successful  
 153 clean-up performance is affinity of the precursor ligand  $L$  to the III-V oxide substrate. We can describe  
 154 formation of one O- $M$  bond and subsequent transformations of the ligand on the sample III-V oxide  
 155 surface (*i.e.* a clean-up process) with the following equation where  $\parallel$  stands for surface bound species  
 156 and  $g$  for gas-phase molecules:



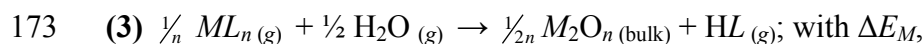
158 In the above equation we assume that the formed metal oxide is stoichiometric: upon increasing the  
 159 coordination number of the metal centre to the native oxide oxygen, the coordination to the ligands



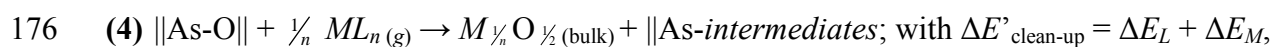
160 decreases and ligands are released to interact with the substrate. The equation also shows that  $M$ -O  
161 formation and interaction of ligands with As can be viewed as separate events, to a first approximation.  
162 Identification of these separate factors allows for an efficient description of interactions of the surface  
163 *intermediates* that are formed as a result of ligand decomposition, and of associated chemical processes  
164 that lead to formation of the clean-up products. Computing the *intermediates* from just one ligand  
165 should be computationally less expensive and easier to understand than computing the decomposition of  
166 the entire precursor molecule. Therefore, in this paper we take advantage of this methodology and  
167 reduce equation (1) to a description of chemical processes associated only with the interaction of one  
168 ligand with the substrate independent of  $M$ , as per the reaction:



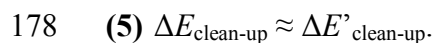
170 A proton is included to ensure overall charge neutrality and so on the right hand side of the reaction a  
171 hydroxyl group  $\|O-H$  is formed. The formation of one  $M$ -O bond in equation (1) can then be described  
172 by the model reaction for various  $M$ :



174 which is the overall ALD reaction. Combination of the ligand reaction (2) and the metal-dependent  
175 correction (3) gives essentially reaction (1):



177 but at much lower computational effort. Therefore:



179 Because of limitations of our current model, we cannot generally compute the complete energetics for  
180 each mechanism here. As we focus in this study on the decomposition of the dma ligand and its redox  
181 properties, our model naturally does not cover molecular or dissociative adsorption of the precursor and  
182 associated steric effects. Nevertheless, for validation purposes we performed explicit simulation of the  
183 dissociative adsorption of the whole precursor molecule according to equation (1). In Table 1 we  
184 compare energetics obtained for adsorption and ligand dissociation for three different precursors:

185 Hf(NMe<sub>2</sub>)<sub>4</sub>, AlMe<sub>3</sub>, TiCl<sub>4</sub>. The ‘whole precursor’ approach gives a  $\Delta E_{\text{clean-up}}$  that agrees well with the  
 186  $\Delta E'_{\text{clean-up}}$  value from the ‘ligand only’ approach in all three cases, thereby strongly supporting the latter  
 187 approach. Additionally the ‘whole precursor’ approach for the Hf(NMe<sub>2</sub>)<sub>4</sub> precursor was used for the  
 188 NEB calculation of activation energies, which is reported in the Results and Discussion section.

189

190 Table 1. Validation of the investigated model: energies  $\Delta E_{\text{clean-up}}$  for reaction of precursor adsorption  
 191 and dissociation of the ligand from the metal center according to reaction  $\parallel\text{As-O}\parallel + \frac{1}{n} ML_n(\text{g}) \rightarrow \parallel\text{O-}$   
 192  $M\frac{1}{n} + \parallel\text{As-L}$  compared to  $\Delta E'_{\text{clean-up}}$  obtained from the model ‘ligand only’ reaction  $\parallel\text{As-O}\parallel + \frac{1}{n} ML_n(\text{g})$   
 193  $\rightarrow M\frac{1}{n} O\frac{1}{2}(\text{bulk}) + \parallel\text{As-L}$ . Surface models showing product of this reaction on the example of Hf[N(Me<sub>2</sub>)<sub>4</sub>  
 194 precursor are available in the supporting information. Simulations were performed using identical  
 195 computational parameters for both approaches.

Metal precursor	$\Delta E_{\text{clean-up}}$ [eV]	$\Delta E'_{\text{clean-up}}$ [eV]
Hf(NMe <sub>2</sub> ) <sub>4</sub>	-1.0	-1.0
AlMe <sub>3</sub>	-1.2	-1.3
TiCl <sub>4</sub>	-0.2	-0.2

196

197 In section 3.1 thermodynamic energies are presented for formation of metal oxides from gas phase  
 198 precursors determined using DFT,  $\Delta E_M$  (equation (3)). In the subsequent sections different types of  
 199 *intermediates* that are formed during clean-up as a result of decomposition of selected precursors are  
 200 examined and their structures are illustrated in Figure 2. Types of reactions included are: dissociation of  
 201 the precursor through scission of the *M-L* bond in section 3.2, decomposition of the dma ligand through  
 202 scission of the C-H and N-C bonds in section 3.3 and multiple decomposition steps combining these  
 203 elementary steps described in section 3.4. Energetics for the interaction of ligands with the substrate,  
 204  $\Delta E_L$ , is given in Table 2. The effectiveness of different metal precursors in performing clean-up of III-V  
 205 oxides is evaluated by correcting  $\Delta E_L$  with  $\Delta E_M$  (also Table 2).  $\Delta E_M$  and  $\Delta E_L$  along with overall  $\Delta E'_{\text{clean-}}$

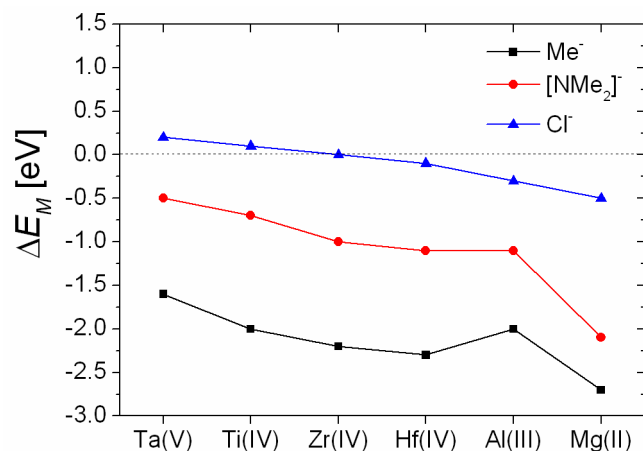
206 up are summarized in Figure 1 and Figure 3. A reaction scheme considered for the decomposition of the  
 207 dma ligand is illustrated in Figure 4. A series of proposed elementary steps can give rise to desorption of  
 208 multiple clean-up products. Based on the thermodynamic accessibility of these elementary surface steps  
 209 and some kinetic indications, we discuss in each section which clean-up mechanism and associated by-  
 210 product is competitive in the ALD process.

## 211 3. Results and Discussion

### 212 3.1. Formation of metal oxides from gas phase precursors

213 Reaction (3) contains information about the reactivity of precursors towards formation of bulk oxide and  
 214 bonding changes upon elimination of ligands as HL. Computed energetics for a selection of metals and  
 215 ligands are summarized and illustrated in Figure 1. Values for reaction (3) can be found in Table 2  
 216 under  $\Delta E^{\text{clean-up}}$  for  $\Delta E_L = 0$  eV (see equations (3) and (4)).

217  
 218 Figure 1. Computed energetics,  $\Delta E_M$ , for formation of metal oxides from gas phase precursors  $ML_n$  ( $x$   
 219 axis:  $M = \text{Mg(II)}, \text{Al(III)}, \text{Ti(IV)}, \text{Zr(IV)}, \text{Hf(IV)}, \text{Ta(V)}$ ;  $L = [\text{N}(\text{Me})_2]^-$ ,  $[\text{Me}]^-$ ,  $[\text{Cl}]^-$ ;  $n =$  oxidation state  
 220 of metal) and water according to:  $\frac{1}{n} ML_n (\text{g}) + \frac{1}{2} \text{H}_2\text{O} (\text{g}) \rightarrow \frac{1}{2n} M_2\text{O}_n (\text{bulk}) + \text{HL} (\text{g})$  (equation (3)). Lines  
 221 are to guide the eye.



222

223

224 The energetics indicate that the most reactive precursor family for formation of metal oxides and  
225 elimination of  $HL$  are metal methyls. The most reactive of the six considered is  $MgMe_2$  with  $\Delta E_M = -2.7$   
226 eV per methyl ligand. The least reactive among the hypothetical methyl precursors is  $TaMe_5$  with  $\Delta E_M$   
227  $= -1.6$  eV per Me for formation of  $Ta_2O_5$ .  $AlMe_3$  with  $\Delta E_M = -2.0$  eV per Me presents similar reactivity  
228 to  $TiMe_4$ , not to  $HfMe_4$  or  $ZrMe_4$ . Al, Hf and Zr alkylamides with  $\Delta E_M \approx -1.0$  eV per ligand have  
229 similar reactivity and the Ta and Ti alkylamides are slightly less reactive. The most reactive for  
230 formation of oxide among metal alkylamides is  $Mg[N(CH_3)_2]_2$  with  $\Delta E_M = -2.1$  eV per alkylamide  
231 ligand. According to our computations the smallest driving force for formation of  $M_2O_n$  is shown by  
232 chloride precursors.  $\Delta E_M$  for  $L = Cl^-$  ranges from  $-0.5$  eV per Cl for Mg to  $+0.2$  eV per Cl for Ta. In  
233 general, the calculations reveal the following order of  $M$  reactivity, insensitive to the identity of  $L$ :  
234  $Mg(II) > Hf(IV) \approx Zr(IV) > Ti(IV) > Ta(V)$ . The exception is Al(III) which is predicted to change its  
235 relative reactivity depending on the nature of  $L$ . Relative to the other metals, the Al cation is the most  
236 reactive when bonded to chloride ligands and the least reactive, with similar reactivity to Ti(IV), for  $L =$   
237  $Me^-$ . These trends are consistent with previous calculations<sup>22</sup>.

238

239

240

241

242

243

244

245

246

247

248

249 Table 2. List of possible clean-up *intermediates*: **A-K**, **A'** and **A''** that are formed during ALD III-V  
 250 substrate exposure to various metal precursors. Energies are in eV relative to  $\|As - O\| + HL_{(g)}$  as per  
 251 reaction (2) with  $L = [N(Me)_2]^-$ ,  $Me^-$ ,  $Cl^-$ . The effect of different  $M = Ta, Ti, Zr, Hf, Al, Mg$  is included  
 252 by adding the correction  $\Delta E_M$  obtained from reaction (3) (see section 2 for details).

$L$	products at surface:	$\Delta E_L$	$\Delta E'_{\text{clean-up}}$ for $M$ :					
			Ta	Ti	Zr	Hf	Al	Mg
	$\ As - O\  + HNMe_{2(g)}$	0.0	-0.5	-0.7	-1.0	-1.1	-1.1	-2.1
$[N(Me)_2]^-$	<b>A</b> $\ O - H + \ As - NMe_2$	+0.1	-0.4	-0.6	-0.9	-1.0	-1.0	-2.0
	<b>B</b> $2\ O - H + \ As - N(Me)CH_2 - As\ $	+0.6	+0.1	-0.1	-0.4	-0.5	-0.5	-1.5
	<b>C</b> $2\ O - H + \ As - N(Me)CH_2 - O\  + 2e^-$	+1.3	+0.8	+0.6	+0.3	+0.2	+0.2	-0.8
	<b>D</b> $\ O - H + \ As - N(Me)CH_2 - As\  + \ As - H - 2e^-$	+2.1	+1.6	+1.4	+1.1	+1.0	+1.0	0.0
	<b>E</b> $\ O - H + \ As - N(Me)CH_2 - O\  + \ As - H$	+1.2	+0.7	+0.5	+0.2	0.1	0.1	-0.9
	<b>F</b> $\ O - H + \ As = NMe + \ O - Me$	+1.5	+1.0	+0.8	+0.5	+0.4	+0.4	-0.6
	<b>G</b> $\ O - H + \ As = NMe + \ As - Me - 2e^-$	+1.6	+1.1	+0.9	+0.6	+0.5	+0.5	-0.5
	<b>H</b> $3\ O - H + \ As - N(CH_2 - As\ )_2$	+1.3	+0.8	+0.6	+0.3	+0.2	+0.2	-0.8
	<b>I</b> $4\ O - H + \ As = NCH=CH_2 + 2e^-$	+2.2	+1.7	+1.5	+1.2	+1.1	+1.1	+0.1
	<b>J</b> $2\ O - H + \ As - N=CH_2 + \ As - Me$	+0.9	+0.4	+0.2	-0.1	-0.2	-0.2	-1.2
	<b>K</b> $3\ O - H + \ As - N=CH - As\  + \ As - Me$	+1.9	+1.4	+1.2	+0.9	+0.8	+0.8	-0.2
$[Me]^-$	$\ As - O\  + CH_{4(g)}$	0.0	-1.6	-2.0	-2.2	-2.3	-2.0	-2.7
	<b>A'</b> $\ O - H + \ As - Me$	+0.7	-0.9	-1.3	-1.5	-1.6	-1.3	-2.0
$[Cl]^-$	$\ As - O\  + HCl_{(g)}$	0.0	+0.2	+0.1	0.0	-0.1	-0.3	-0.5
	<b>A''</b> $\ O - H + \ As - Cl$	-0.3	-0.1	-0.2	-0.3	-0.4	-0.6	-0.9

253

### 254 3.2. Dissociation of ligand by M-L scission

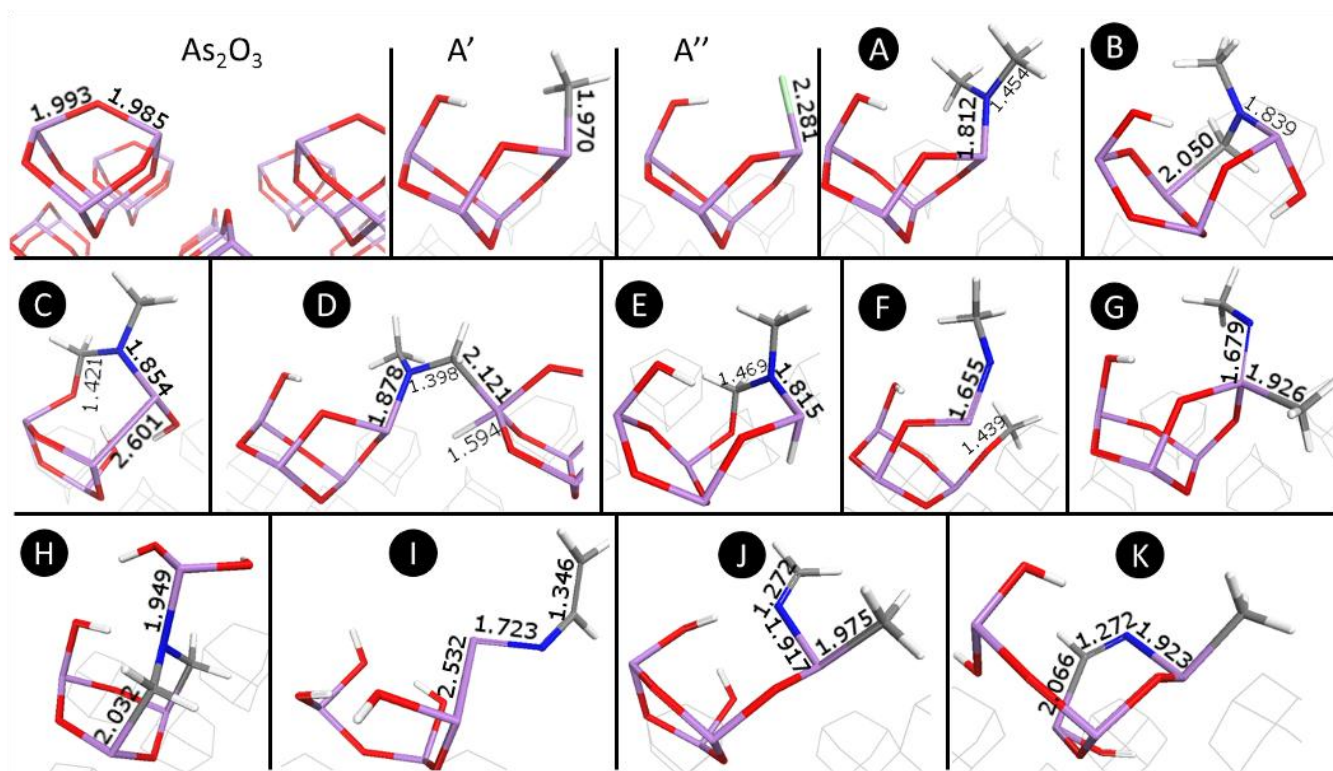
255 By calculating DFT energies for dissociation of the ligand from the metal center, we investigate the  
 256 affinity of the ligand to the oxide to be cleaned-up. This gives us  $\Delta E'_{\text{clean-up}}$  for the elementary step that  
 257 leads to a ligand exchange mechanism. The elementary steps that we have considered involve the  
 258 transfer of a dimethylamide, methyl and chloride group to the surface As atom in structures **A**, **A'** and

259 A'' respectively, shown in Figure 2. Energetics for formation of intermediate **A** show that the  
 260 alkylamide ligand can readily dissociate from the *M* center to the available As site and form a  
 261 thermodynamically stable product ||As – N(CH<sub>3</sub>)<sub>2</sub> plus oxide of *M* (see Table 2 and Figure 3 for  
 262 energetics). According to reaction (2) and correction for the *M*-O bond formation, reaction (3), this  
 263 ligand transfer process is exothermic for all considered metals. The energy for this reaction ranges from  
 264 -0.4 eV per ligand for Ta[N(CH<sub>3</sub>)<sub>2</sub>]<sub>5</sub> to -2.0 eV for Mg[N(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>. This reaction is very facile with a  
 265 computed activation energy of just +0.1 eV, and so it will proceed until the surface is saturated with ||As  
 266 – N(CH<sub>3</sub>)<sub>2</sub> species (the reaction profile for the corresponding reaction of the whole precursor is  
 267 available in the supporting information).

268

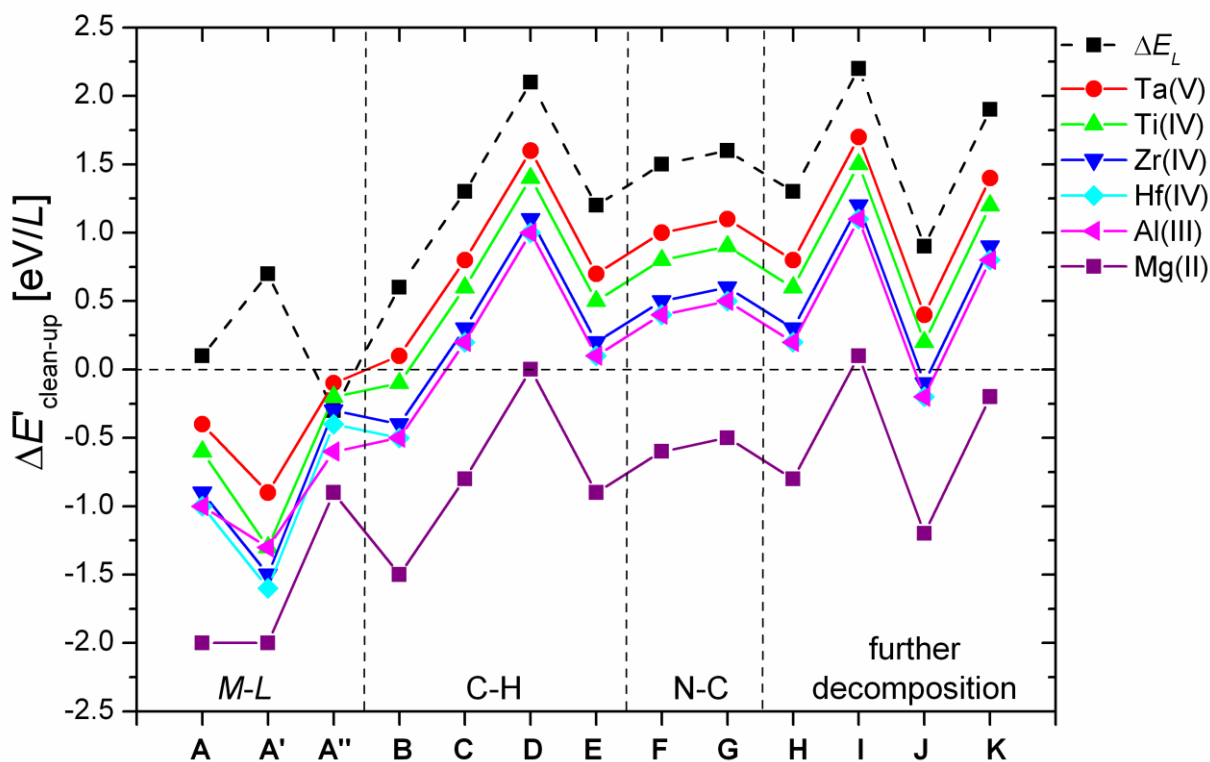
269 Figure 2. Surface models for As<sub>2</sub>O<sub>3</sub> and decomposition species of metal methyls, **A'**, metal chlorides,  
 270 **A''**, and metal alkylamides, **A-K**. Stick representation: purple As, red O, white H, gray C, green Cl,  
 271 blue N. Selected bond lengths are given in Å. Thin lines show adjacent substrate atoms.

272



273

274 Figure 3. Computed energetics for surface intermediates, **A-K**, which are formed during clean-up of  
 275  $\text{As}_2\text{O}_3$ . As listed in Table 2, **A**, **A'** and **A''** are surface products of precursor decomposition through  
 276 scission of  $M-L$  bond ( $M = \text{Mg(II)}$ ,  $\text{Al(III)}$ ,  $\text{Ti(IV)}$ ,  $\text{Zr(IV)}$ ,  $\text{Hf(IV)}$ ,  $\text{Ta(V)}$ ) for  $L = [\text{N}(\text{Me})_2]^-$ ,  $[\text{Me}]^-$ ,  
 277  $[\text{Cl}]^-$  respectively; **B-E** are surface products of decomposition of  $[\text{N}(\text{Me})_2]^-$  through scission of C-H  
 278 bond; **F** and **G** surface products of decomposition of  $[\text{N}(\text{Me})_2]^-$  through scission of N-C bond; **H-K** are  
 279 surface products when further decomposition occurs through scission of both C-H and N-C bonds.  $\Delta E_L$   
 280 (equation (2)) describes interaction of the ligand  $L$  with the  $\text{As}_2\text{O}_3$  substrate (black datapoints). It is  
 281 subsequently corrected with  $\Delta E_M$  (equation (3)) and gives overall  $\Delta E'_{\text{clean-up}}$  for various  $M$  (equation  
 282 (4)). Lines are to guide the eye and do not imply a reaction sequence (see instead Figure 4).



283  
 284 Energetics show that the methyl ligand is very reactive towards the arsenic oxide substrate and more  
 285 reactive than alkylamide (**A'** Figure 3). The energy ranges from -0.9 eV for  $\text{Ta}(\text{CH}_3)_5$  to -2.0 eV for  
 286  $\text{Mg}(\text{CH}_3)_2$ . The energy for exchange of a  $\text{Cl}^-$  ligand between the precursor metal center and the native

287 oxide, with product A'' in Figure 2, ranges from -0.1 eV for TaCl<sub>5</sub> to -0.9 eV for MgCl<sub>2</sub>, indicating that  
288 it is less thermodynamically favored than for alkylamides and methyls.

289 Sufficient concentration of these As – L groups may lead to formation of AsL<sub>3</sub>:  
290 tris(dimethylamino)arsine, TDMAAs, As[N(CH<sub>3</sub>)<sub>2</sub>]<sub>3</sub>; trimethylarsine, As(CH<sub>3</sub>)<sub>3</sub> and arsenic trichloride  
291 AsCl<sub>3</sub>, as volatile products in processes utilizing alkylamides, methyl and chloride precursors  
292 respectively. Desorption of these molecules means that As<sub>2</sub>O<sub>3</sub> has been transformed into M<sub>2</sub>O<sub>n</sub>, *i.e.*  
293 clean-up. Indeed, this ligand transfer mechanism has been proposed by others <sup>3a, 8</sup> to explain the clean-  
294 up effect. Experimental study clearly shows enhancement of the clean-up process with increasing  
295 temperature when metal alkylamides are used <sup>5, 23</sup>. Even though the first step of the ligand exchange  
296 reaction is extremely facile, both thermodynamically and kinetically, significant kinetic requirements  
297 may originate from steric effects in subsequent steps. There was evidence for this in our previous study  
298 for TMA, where we showed that the rate limiting step for the ligand transfer process could be crowding  
299 of methyl ligands at one surface site <sup>24</sup>. We suspect that this process can be even more difficult for the  
300 bulkier alkylamides. Thus, steric effects may have a pronounced influence on the kinetics of ligand  
301 transfer to TDMAAs, which may stop this reaction before going to completion, and promote ligand  
302 decomposition instead. In fact, TDMAAs is known to thermally decompose on the GaAs surface <sup>25</sup>.  
303 Therefore, it is reasonable to suspect that the alkylamide can decompose, or partially decompose, in  
304 contact with the native oxide surface, and give rise to other clean-up products rather than form  
305 TDMAAs. Ligand decomposition is investigated in subsequent sections.

306 In the case of chlorides, although they are successfully used in ALD of different metal oxides, there is  
307 no agreement in the literature about their interfacial self-cleaning abilities <sup>3b, 4a, 10</sup>. One reason may be  
308 the lower driving force towards formation of the metal oxide dielectric; Figure 1 shows that formation  
309 of the metal oxide during clean-up is an important factor in case of alkylamides and methyls, but a  
310 minor factor in the case of chlorides ( $\Delta E_M$  ranges +0.2 to -0.5 eV). Therefore, we suggest that chloride  
311 chemistry is different. Most of the metal chlorides are weak Lewis acids. Their electrophilic



312 characteristic allows them to form Lewis adducts like TaOCl<sub>3</sub>, complexes like [TiCl<sub>6</sub>]<sup>2-</sup> or even  
313 hydrates, *e.g.* MgCl<sub>2</sub>(H<sub>2</sub>O)<sub>x</sub><sup>26</sup>. Formation of oxychlorides, *e.g.* TiOCl<sub>2</sub>, or even hydroxychlorides,  
314 TiCl<sub>3</sub>OH, during clean-up with TiCl<sub>4</sub> for TiO<sub>2</sub> deposition, could explain observed removal of O and  
315 surface passivation with Cl<sup>4a</sup>. As proposed before, clean-up with this ligand can be accounted for via an  
316 agglomeration reaction mechanism<sup>3b</sup>.

317 Ligand affinity for Ga and In is discussed in section 3.5 .

### 318 *3.3. Decomposition of dma ligand*

319 For the following consideration of decomposition processes of alkylamide ligand on the example of  
320 dimethylamide we use the highly stable product A ||As – N(CH<sub>3</sub>)<sub>2</sub>, as a starting species for further clean-  
321 up transformations **B-K**. Decomposition of the alkylamide ligand is possible via activation of a C-H  
322 bond, releasing anionic or cationic H, or of an N-C bond, releasing anionic or cationic CH<sub>3</sub> as  
323 schematically shown in Figure 4. In this section we examine mechanistic paths for these H and CH<sub>3</sub>  
324 moieties to attack As and O sites. We consider all possible reactions and highlight redox processes that  
325 may enhance the clean-up effect.

326

327

328

329

330

331

332

333

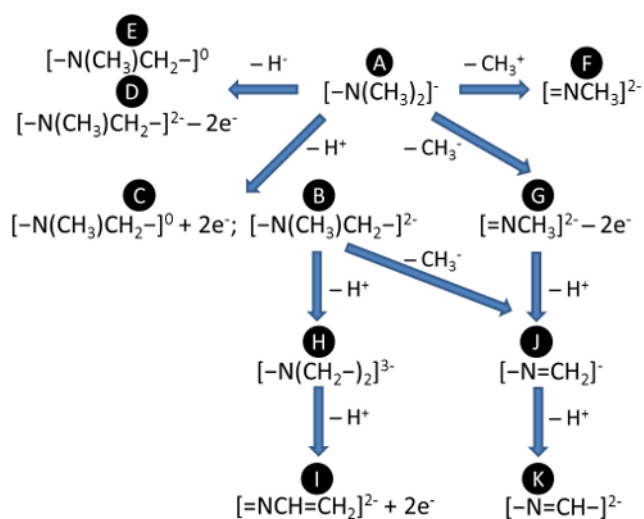
334

335

336

337

338 Figure 4. Reaction scheme for decomposition of dimethylamido ligand  $[-N(CH_3)_2]^-$  on metal oxide  
 339 surfaces (species **A-K**). Notation: ‘ $-H^{+/-}$ ’ means dissociation of proton/hydride from ligand to the  
 340 surface; ‘ $-Me^{+/-}$ ’ means dissociation of methylum/methanide group from ligand to the surface; ‘ $+2e^-$ ’  
 341 means oxidation of ligand by surface (reduction of surface by ligand); ‘ $-2e^-$ ’ means reduction of ligand  
 342 by surface (oxidation of surface by ligand).



343

### 344 3.3.1. C-H scission and H elimination (B-E)

345 The C-H bond of the ligand is weakened by the electron density of the lone pair of electrons on the  
 346 neighboring N atom, so that H  $\alpha$  to the N atom can dissociate and bond to an available surface site. First  
 347 we investigate scission of the C-H bond and formation of an O-H bond in the intermediate **B** shown in  
 348 Figure 2. Our calculations show that upon the proton ( $H^+$ ) transfer from a ligand to a surface O atom,  
 349 the As-O bond is broken. The electronic density around the C atom in the remaining methylene ( $CH_2$ )  
 350 moiety of the ligand increases by  $\Delta q = +1.5e$ . This Lewis basic C atom can interact with the surface As  
 351 cation that lost coordination to the O atom. The bond formed between the As atom and the C atom is 2.0  
 352 Å long which is typical of single As-C bond. As a result a N-methylmethylenimido ion ( $[-N(Me)CH_2-$   
 353  $]^{2-}$ ) is attached to the surface. Our attempts to find a competitive minimum for the N-  
 354 methylmethylenimido ligand with tricoordinated N atom featuring a N=C double bond (*i.e.*  $[-$   
 355  $N(Me)=CH_2]^-$ ) were not successful. The thermodynamically stable state preserves tricoordinated N and  
 356 tetrahedral C. This process is the most exothermic of the decomposition processes with a calculated

357  $\Delta E'_{\text{clean-up}}$  ranging from +0.1 eV for Ta[N(CH<sub>3</sub>)<sub>2</sub>]<sub>5</sub> to -1.5 eV for Mg[N(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (Table 2, **B**). An  
358 activation energy of around +1.4 eV is computed for the example of Hf[N(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub> where  $\Delta E'_{\text{clean-up}} =$   
359 0.5 eV (the reaction profile for the corresponding reaction of the whole precursor is available in the  
360 supporting information).

361 We also examine the redox process mediated by ligand attack of the CH<sub>2</sub> moiety onto the O site, instead  
362 of the As site, to form product **C** (Figure 2). This is analogous to the migration of CH<sub>3</sub> from As to O that  
363 we observed to be responsible for clean-up with TMA<sup>14</sup>. In this elementary step two As-O bonds are  
364 broken, promoting formation of the O-H (1.0 Å) bond and the O-C bond (1.4 Å). Two electron-deficient  
365 surface metal cations are forced to interact and as a result a metallic As-As dimer is formed along with  
366 the intermediate ||As – NCH<sub>3</sub>CH<sub>2</sub> – O||. Electrons are transferred to surface arsenic (+1.0e and +1.1e on  
367 the dimer atoms) from the C atom of CH<sub>2</sub> (-1.6e) but also from N (-0.5e), elongating the N-As bond by  
368 around 2% as compared to structure **A**. Decomposition of the alkylamide via this process is thus  
369 reducing the As oxide surface and contributing to clean-up. This oxidation of the C atom is endothermic  
370 for most of the precursors: tantalum, titanium, zirconium amides (+0.8, +0.6, +0.3 eV respectively),  
371 almost neutral for hafnium amide (+0.1 eV) and exothermic for magnesium amide (-0.8 eV) according  
372 to equations (2) + (3) ( $\Delta E'_{\text{clean-up}}$ , Table 2). It is less favorable than formation of the As-C bond in the  
373 structure **B** described above.

374 For completeness we studied scission of the C-H bond and the transfer of H to an As site. This process  
375 essentially involves hydride (H<sup>-</sup>) dissociation from the alkylamide ligand and formation of products **D**  
376 and **E** with structures illustrated in Figure 2. In the intermediate **D** two new bonds are created: As-H and  
377 As-C, increasing the coordination number of the As atom from three to five. Formation of these two  
378 bonds is expected to cause the withdrawal of the electronic density from the oxide substrate and so its  
379 local oxidation (see scheme in Figure 4). Charge analysis suggests a decrease in electronic populations  
380 by only -1.0e on the oxidised pentacoordinated As and an increase of +1.0e on the H atom bonded to  
381 this arsenic. The absence of charge transfer between this arsenic and CH<sub>2</sub> suggests some charge  
382 retraction that is explained as follows. The CH<sub>2</sub> moiety of the created surface product ||As – N(Me)CH<sub>2</sub>

383 – As|| becomes more Lewis acidic ( $-0.4e$  on the C atom) and the N atom more Lewis basic ( $+0.5e$ ),  
384 attracting each other (4% shorter N-CH<sub>2</sub> bond, relative to the same bond in **B**) and repelling bonded  
385 arsenic atoms (both: As-N and As-CH<sub>2</sub> bonds are elongated by 4%, relative to the same bonds in **B** or  
386 **C**). This indicates that desorption of the N-methylmethylenimido ligand as neutral Me-N=CH<sub>2</sub> should  
387 be preferred over formation of the dianion ( $[-N(Me)CH_2]^{2-}$  and substrate oxidation. The oxidation of  
388 As upon hydride dissociation is not favorable. In fact this is one of the least favorable processes that we  
389 have computed with energy ranging from +1.6 eV to +1.0 eV for almost all of the precursors and  
390 energetically neutral only for Mg[N(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>. We observe that no As-O bond is broken in this  
391 elementary process, *i.e.* it does not contribute to clean-up.

392 Our results indicate that energy for hydride dissociation can be lowered by 0.9 eV when this process is  
393 accompanied by oxidation of the C atom and formation of the surface product **E**: ||As – NCH<sub>3</sub>CH<sub>2</sub> – O||  
394 + ||As – H. In this case As-H and O-C bonds are formed breaking one As-O bond (see Figure 2). We  
395 note that electronic densities are withdrawn from the O-CH<sub>2</sub>-N entity ( $-1.0e$ ) by the newly-formed  
396 hydride ( $+1.0e$ ) and there is no charge transfer to the substrate. The attack of CH<sub>2</sub> onto the O site and  
397 transfer of H<sup>-</sup> to the As site is slightly endothermic for most of the precursors (+0.7 to +0.1 eV) and  
398 exothermic for the magnesium precursor ( $-0.9$  eV).

399 DFT calculations show that decomposition of alkylamide ligand through scission of the C-H bond  $\alpha$  to  
400 N is thermodynamically feasible, but requires quite high activation energy. This pathway is often  
401 referred to in the literature as  $\beta$ -H elimination<sup>27</sup>. Most likely this process will result in hydroxylation of  
402 the native oxides and formation of C-As(Ga, In) bonds (**B**). A possible volatile product of this clean-up  
403 transformation is N-methyl methyleneimine (MMI). Desorption of imine in the considered system  
404 requires reorganization in the electronic density with the formation of an N=C double bond and  
405 cleavage of As-N and As-C bonds, which is consistent with a high activation energy (+1.4 eV for the Hf  
406 case; see above). Simultaneously, charge transfer to the surface As should occur resulting in formation  
407 of metallic As-As bonds. We calculate that desorption of imine according to the reaction: ||As –

408  $\text{NCH}_3\text{CH}_2 - \text{As}|| \rightarrow ||\text{As-As}|| + \text{CH}_3\text{NCH}_2 (g)$  costs +0.7 eV relative to formation of **B**. Thus, the  
409 computed reaction energies and high activation energy for the first step suggest that this clean-up  
410 pathway producing imine needs elevated temperature for activation.

411 The weakening effect of the N-lone pair on the C-H bonds in the  $\alpha$  position has been observed in  
412 vibrational spectroscopy, where an unusually low frequency of vibration of the C-H mode in TDMAH  
413 has been reported<sup>28</sup>. The C-H dissociation is possible already upon adsorption of alkylamide precursors  
414 onto silicon substrates at very low temperature of 220 K<sup>29</sup>. As mentioned in the previous section MMI  
415 is a detected product of etching GaAs surface by TDMAAs<sup>25a</sup>. Several reports can be found where  
416 metal alkylamides are shown to decompose to produce imine and amine<sup>30</sup>. We show here that H  
417 elimination can occur from a ligand that has migrated to the native oxide surface (**A**  $\rightarrow$  **B**). Product **B**  
418 can then undergo other transformations **B**  $\rightarrow$  **H-K**, leading to different clean-up products as described  
419 later, or desorption of imine can occur. Either process leads to arsenic oxide removal and/or reduction to  
420 metallic arsenic, and so may contribute to the clean-up effect.

421 Another clean-up product that can arise from H elimination in the structures **D** and **E** is arsine,  $\text{AsH}_3$ .  
422 However, the unfavourable energetics computed by DFT for elementary steps leading to surface  
423 functionalization with  $||\text{As} - \text{H}$  groups suggests that formation of arsine from intermediate **D** or **E** is a  
424 minor clean-up channel.

### 425 *3.3.2. N-C scission (F-G)*

426 We next examined possible pathways for  $\text{CH}_3$  dissociation resulting with products **F** and **G** (for  
427 pathways see Figure 4, for structures of products Figure 2). First we considered activation of the N-C  
428 bond in the presence of the available Lewis basic O site of the substrate (**F**). As the  $\text{CH}_3$  group  
429 coordinated to the N atom in the alkylamide ligand has Lewis acidic character (formally  $\text{CH}_3^+$ ,  
430 methylium cation), we expect no redox during transfer to the substrate in this step. Upon this transfer  
431 the As-O bond is broken, promoting formation of a double bond between the As and N atoms (1.7 Å).  
432 Our results indicate that the reaction along this pathway is moderately endothermic with a

433 thermodynamic energy of +1.0 to +0.4 eV for Ta, Ti, Zr, Hf, Al precursors and exothermic by -0.6 eV  
434 for the Mg precursor ( $\Delta E'_{\text{clean-up}}$ , Table 2).

435 Another possibility is for the CH<sub>3</sub> moiety to attack an As surface site (**G**). The DFT calculations show  
436 that, similarly, an As=N double bond is formed, but As-O bonds are not affected. We observe oxidation  
437 of the As atom (-1.9e), which is now pentacoordinated, and reduction of the C atom of the dissociated  
438 CH<sub>3</sub> moiety (+1.9e), consistent with transfer as CH<sub>3</sub><sup>-</sup> (methanide anion). This elementary step is  
439 therefore the reverse of clean-up. The bond formed between the C atom and the As atom is 1.9 Å long.  
440 This decomposition structure is a little more unstable than **F** with respect to reactants, at a calculated  
441 energy difference of +0.1 eV relative to the energy for formation of product **F**.

442 Pathways involving dissociation of the methyl group lead to functionalization of the surface with ||O –  
443 CH<sub>3</sub> (**F**) or formation of the ||As – CH<sub>3</sub> groups (**G**) along with the ||As = NCH<sub>3</sub> fragment. This can thus  
444 lead to desorption of gaseous dimethyl ether, O(CH<sub>3</sub>)<sub>2</sub>, or trimethylarsine, As(CH<sub>3</sub>)<sub>3</sub>. Additionally, if a  
445 source of protons is present, methane CH<sub>4</sub> can be formed from ||As – CH<sub>3</sub>. However, our calculations  
446 show that elementary steps for **F** and **G** formation that could give dimethyl ether or trimethylarsine as  
447 clean-up products are less competitive when compared to the elementary steps leading to formation of  
448 TDMAAs or MMI (**A** or **B**, see Table 2). During ALD of metal oxide films, protons can derive from the  
449 H<sub>2</sub>O pulse, but are supposedly eliminated in reaction with alkylamide ligands to produce amine, the  
450 main ALD product. ||O-H groups are also formed during the H elimination process investigated above.  
451 We will see later that the sequence of production of **B** and **G** *intermediates* is competitive and can  
452 directly lead to methane production.

### 453 *3.4. Further decomposition of dma ligand*

#### 454 *3.4.1. Multiple redox steps – dehydrogenation H-I*

455 Based on the results shown above, we assume that the main reaction channel for the elimination of H  
456 atoms from alkylamide ligands on the oxide substrate is formation of the surface hydroxide and carbon-  
457 arsenic bound *intermediate* as in product **B**. In this section we investigate the most stable products of  
458 successive dehydrogenation of the alkylamide ligand.

459 The stability of the surface intermediate **H** decreases by about 0.7 eV relative to **B** after a second proton  
460 transfer. The electronic density increases on both C atoms (+1.2e and +1.3e) and a total of two protons  
461 are transferred to the oxide surface. There are now two CH<sub>2</sub> entities that form bonds with acidic As  
462 atoms through basic C atoms. A loss of electronic density on N of -0.5e is observed in Bader analysis.  
463 This affects the As-N bond, which is weakened (about 8% longer than the As-N bond in product **B**)  
464 suggesting that the  $\pi$  character of this bond decreases. The lone pair of electrons on N is no longer  
465 stabilized and N becomes nearly pyramidal in this structure (see Figure 2). This process requires energy  
466 and so it is clear that it requires some thermal activation.

467 Further dehydrogenation is possible via carbon disproportionation yielding a methyldiyne fragment  
468 (HC) that inserts into the C-N bond in the intermediate **I**. The surface product features a double bond  
469 between As and N (1.7 Å) that is now bound to a vinyl moiety CH=CH<sub>2</sub> (C=C bond length: 1.3 Å).  
470 Three hydroxide groups and an As-As dimer with the bond length of 2.5 Å are formed at the expense of  
471 four As-O bonds. Bader analysis confirms reduction of the dimer As atoms (+1.1e and +1.4e for the As  
472 atoms bound to N) which means that this reaction contributes to clean-up. We also observe  
473 disproportionation of charge between C atoms (increase of electronic population on methylene group of  
474 +0.6e and decrease on methyldiyne group of -0.3e relative to populations on methyl groups in amide  
475 ligand in structure **A**). We note some charge transfer to the N atom of +0.5e. Formation of an  
476 [=NCH=CH<sub>2</sub>]<sup>2-</sup> adsorbate is the most endothermic of the considered processes (+1.6 eV relative to **B**  
477 formation).

478 Our computations thus show that successive dehydrogenation becomes progressively less favored. It  
479 may result in the formation of the following volatile products: imine from species **B** as mentioned  
480 above; aziridine, HN(CH<sub>2</sub>)<sub>2</sub>, from **H**; ethylene, C<sub>2</sub>H<sub>4</sub>, and subsequently molecular nitrogen, N<sub>2</sub>, from **I**.  
481 The energetics for pathways leading to desorption of these species suggest that this is only possible  
482 through thermal activation – moderate temperatures for imine formation and high temperatures for  
483 desorption of molecular nitrogen.

484 Aziridine may be produced from structure **H** by a reaction of cleaving As-C bonds, forming a C-C bond  
485 (for this process we calculate +0.5 eV relative to formation of **H**), subsequent coupling with adjacent  
486 protons if available and desorption, all of which has a DFT energy of just +0.3 eV relative to **H**. This  
487 contributes to clean-up, leaving the surface with metallic As-As bonds according to:  $\parallel\text{As} - \text{N}(\text{CH}_2 -$   
488  $\text{As}\parallel)_2 + \parallel\text{O} - \text{H} \rightarrow \parallel\text{As} - \text{O}\parallel + \parallel\text{As} - \text{As}\parallel + \text{HN}(\text{CH}_2)_2 (g)$ . The rate limiting step may be breaking As-C  
489 and forming a three membered C-C-N ring. Aziridine is one of the stable products detected in the *in situ*  
490 mass spectroscopy experiment of thermal decomposition of TDMAAs below 450°C<sup>30b</sup>.

491 C<sub>2</sub>H<sub>4</sub> was detected as a desorption product originating from secondary surface reactions when a  
492 tantalum surface was exposed to Ta[N(CH<sub>3</sub>)<sub>2</sub>]<sub>5</sub> at 550 K<sup>27</sup>. One of the proposed mechanisms envisages  
493 dehydrogenation of methyleneimido intermediates, insertion of a methyldiyne moiety into the carbon-  
494 nitrogen bond and subsequent hydrogenation of the vinyl fragment to produce ethylene and leave an  
495 adsorbed N atom<sup>27</sup>. We suggest that, on the reducible arsenic oxide substrate following coupling of  
496 adsorbed N atoms to form N<sub>2</sub> could be possible at highly elevated temperatures, which would result in  
497 clean-up according to:  $2 \parallel\text{As} = \text{NCH}=\text{CH}_2 + 2 \parallel\text{O} - \text{H} \rightarrow \parallel\text{As} - \text{As}\parallel + 2 \text{C}_2\text{H}_4 (g) + \text{N}_2 (g)$ .

#### 498 **3.4.2. Multiple redox steps J-K**

499 In this section we study sequences of CH<sub>3</sub> dissociation and alkylamide dehydrogenation reactions that  
500 give rise to new clean-up products. Assuming, as previously, that the most probable pathway for  
501 alkylamide dehydrogenation is arsenic oxide hydroxylation, we can consider pathways where the CH<sub>3</sub>  
502 group formally dissociates either as the methylium cation or as the methanide anion (as the above  
503 investigation of processes producing **F** and **G** revealed a competition between them). Here we show the  
504 most stable products of these reactions. All other possible reactions can be found in the supporting  
505 information.

506 Our investigations suggest that the more stable products are those formed during reactions that do not  
507 involve charge transfer to the oxide substrate. For instance, dehydrogenation of the alkylamide ligand  
508 followed by dissociation of the methanide anion in structure **J** (Figure 1) is preferred over dissociation  
509 of the methylium cation that combined with proton dissociation results in substrate reduction: [–



510  $\text{N}(\text{CH}_3)_2^- \rightarrow [-\text{N}=\text{CH}_2]^- + [\text{CH}_3]^+ + [\text{H}]^+ + 2e^-$  (not showed in Figure 1). The step leading to product **J**  
511 among the few steps that we find to be exothermic or neutral at 0 K for most of the regarded precursors  
512 (Table 2). The reorganized electron density in the proton dissociation process (see section 3.3.1 for  
513 description of the proton elimination process in structure **B**) can be attracted by a  $\text{CH}_3$  group instead of a  
514  $\text{CH}_2$  group. Bader analysis shows an increase in the electronic populations on the C atom of  $\text{CH}_3$   
515 ( $+1.9e$ ) and decrease on the C atom belonging to the methylene moiety ( $-1.2e$ ). The acidic methylene  
516 forms a double bond with the N atom (1.3 Å), instead of bonding to surface cation like in structure **B**.  
517 The basic methanide bonds with the As atom (2.0 Å). We note some increase of electronic density on  
518 the N atom that is now even more basic ( $+0.5e$ ) than in the original alkylamide ligand in structure **A**.  
519 Proton dissociation accompanied by the formation of the methanide anion could be a low temperature  
520 channel for the formation of  $\text{CH}_4$ . According to our computations formation of methane from surface  
521 intermediate **J** is slightly exothermic with energy  $-0.1$  eV (neglecting entropy).  $\text{CH}_4$  was observed in  
522 some studies as a product of decomposition of the amido ligands. Infrared (IR) spectroscopy and  
523 temperature-programmed desorption (TPD) investigations of  $\text{Ti}[\text{N}(\text{CH}_3)_2]_4$  on a Si substrate showed that  
524 methane desorbs at temperatures below 400 K <sup>29b</sup>. In the same study DFT calculations suggest that  
525 facile generation of methane right above room temperature is due to the surface activation of C – H and  
526 C – N bonds of amido ligand. In the thermal chemistry investigation of  $\text{Ta}[\text{N}(\text{CH}_3)_2]_5$   $\text{CH}_4$  is a  
527 decomposition product detected throughout the studied temperature range up to 600 K <sup>27</sup>. Our DFT  
528 results suggest that scission of the N-C bond is triggered by the H elimination process on the oxide  
529 substrate and thermodynamically is not as demanding as other decomposition processes. Although  
530 formation of methane is plausible, desorption of this chemical alone from the oxidised III-V system  
531 does not directly result in self-cleaning. In this pathway methane is formed according to:  $\|\text{As} - \text{Me} + \|\text{O}$   
532  $- \text{H} \rightarrow \|\text{As} - \text{O}\| + \text{CH}_4$ , so arsenic oxygen bonds are formed. However, other products can arise as a  
533 consequence of saturation of the native oxide surface with  $[-\text{N}=\text{CH}_2]^-$  groups after  $\text{CH}_4$  desorption in  
534 species **J**:  $\text{C}_2\text{H}_4$  and subsequently  $\text{N}_2$ . Eventual desorption of  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$  and  $\text{N}_2$  would finally lead to  
535 clean-up resulting in reduction of arsenic oxide to metallic arsenic, but involving multiple redox steps: 2

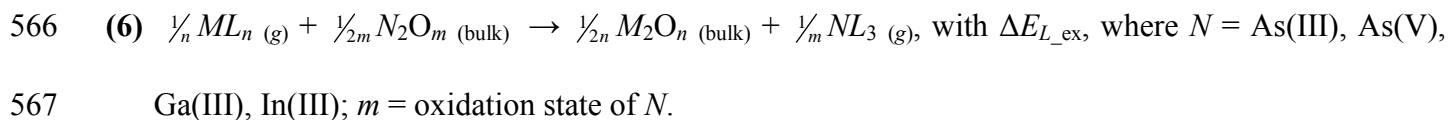
536  $\parallel\text{As} - \text{N}=\text{CH}_2 \rightarrow \parallel\text{As} - \text{As}\parallel + \text{C}_2\text{H}_4_{(g)} + \text{N}_2_{(g)}$ . This process requires energy to break the double bond  
537 between N and C atoms, combining two  $\text{CH}_2$  groups and two N moieties on the surface. As remarked in  
538 our discussion of possible products arising from *intermediate I*, processes involving multiple redox  
539 steps are presumably possible at highly elevated temperatures.

540 Further dehydrogenation of the methylene group in the  $[-\text{N}=\text{CH}_2]^-$  adsorbate described above, yields a  
541 methylidyne ( $\text{CH}^+$ ) ion in surface product **K**. This is less favored by +1.0 eV relative to previous  
542 process **J** (see Table 2). Proton dissociation to another O site renews C basicity (+1.0e with respect to  
543 the  $[-\text{N}=\text{CH}_2]^-$  adsorbate) that now can attack another As site. The  $[-\text{N}=\text{CH}-]^{2-}$  ion is bound to surface  
544 arsenic atoms through N and C, forming bonds 1.9 Å and 2.0 Å long respectively (**K** Figure 1).  
545 Generation of the  $[-\text{N}=\text{CH}-]^{2-}$  surface intermediate can directly lead to desorption of hydrogen cyanide,  
546 HCN, another clean-up product:  $\parallel\text{As} - \text{N}=\text{CH} - \text{As}\parallel \rightarrow \parallel\text{As} - \text{As}\parallel + \text{HCN}_{(g)}$ . HCN was detected to  
547 desorb at 600 K during tantalum alkylamide exposure to a tantalum substrate<sup>27</sup>.

### 548 *3.5 Effect of substrate on clean-up*

549 Our model supposes that clean-up can be achieved by successive dissociation of ligands from the  
550 absorbed precursor. One can expect that the  $M - L$  bond can be easily activated on the oxide surface  
551 when the substrate metal oxide is less stable than the deposited metal oxide  $M_2O_n$ . The metal center of  
552 the precursor then becomes chemically active towards penetrating the III-V oxide substrate and  
553 scavenging the oxygen. A similar technique is used for equivalent-oxide-thickness scaling for  
554 complementary metal–oxide–semiconductor devices<sup>31</sup>. With different variations scaling is achieved via  
555 a scavenging reaction between the scavenging element (metal) and  $\text{SiO}_2$  and the driving force is also  
556 formation of the metal oxide rather than maintaining  $\text{SiO}_2$ . We showed previously that the driving force  
557 of the clean-up effect is removing  $\text{As}(\text{Ga}, \text{In}) - \text{O}$  bonds and forming  $M - \text{O}$  bonds<sup>14, 31</sup>. As has lower  
558 electropositivity and therefore lower affinity to O than the metals considered: Mg, Hf, Zr, Ti, Ta and Al.  
559 In thermodynamic equilibrium, formation of any of the oxides of these metals is assumed to be favored  
560 over formation of the As oxide. DFT energetics for the ligand exchange mechanism supports this  
561 supposition, independent of the ligand in use (see Figure 3 **A**, **A'** and **A''**). Among the III-V elements

562 (As, Ga, In) it is again As that has the lowest electropositivity and forms the weakest oxides. To  
563 emphasize this we calculate from first principles bulk energies for ligand exchange between the  
564 regarded precursors and Ga(III) and In(III) native oxides and compare them with the exchange energy  
565 for As(III/V) native oxide:



568 Figure 5 shows the energetics for the above reaction on the example of alkylamide precursors ( $L =$   
569  $[\text{NMe}_2]$ ). It is clearly seen that  $\text{As}_2\text{O}_3$  is the weakest and the most reactive among these native oxides  
570 towards exchanging O with ligands and therefore is the easiest to clean-up. It seems that In oxide resists  
571 clean-up more than Ga oxide and is less likely to bind to ligands at the surface. As(III) and As(V) oxides  
572 are seen to have similar reactivity for ligand exchange, with the exception of  $\text{Al}[\text{NMe}_2]_3$  that seems to  
573 have greater affinity for As(III). We observe no oxidation state dependency for the ligand exchange  
574 mechanism, contrary to the suggestion of Hinkle *et al*<sup>8</sup>. This result holds true for different ligands (see  
575 supporting information).

576

577

578

579

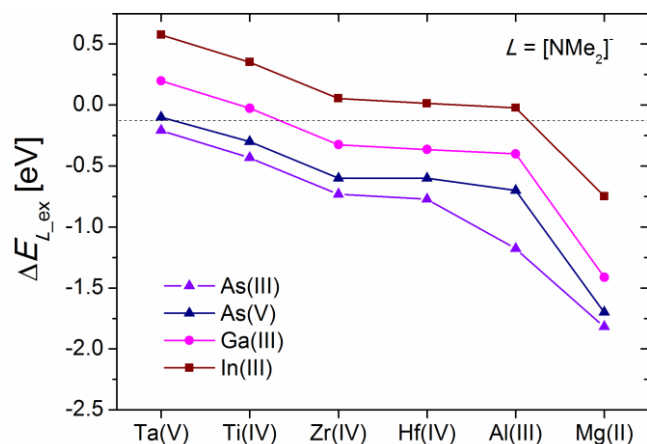
580

581

582

583

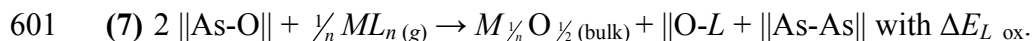
584 Figure 5. Computed energetics for ligand exchange of alkylamide between precursor metal center and  
 585 bulk III-V oxide:  $\text{As}_2\text{O}_3$ ,  $\text{As}_2\text{O}_5$ ,  $\text{Ga}_2\text{O}_3$  and  $\text{In}_2\text{O}_3$  according to:  $\frac{1}{n}ML_n(g) + \frac{1}{2m}N_2O_m(\text{bulk}) \rightarrow \frac{1}{2n}M_2O_n$   
 586  $(\text{bulk}) + \frac{1}{m}NL_3(g)$  for  $M = \text{Mg(II)}$ ,  $\text{Al(III)}$ ,  $\text{Ti(IV)}$ ,  $\text{Zr(IV)}$ ,  $\text{Hf(IV)}$ ,  $\text{Ta(V)}$ ,  $L = [\text{N}(\text{Me})_2]^-$ ;  $n =$  oxidation  
 587 state of  $M$ ;  $N = \text{As(III)}$ ,  $\text{As(V)}$ ,  $\text{Ga(III)}$ ,  $\text{In(III)}$ ;  $m =$  oxidation state of  $N$ . Lines are to guide the eye.



588

589

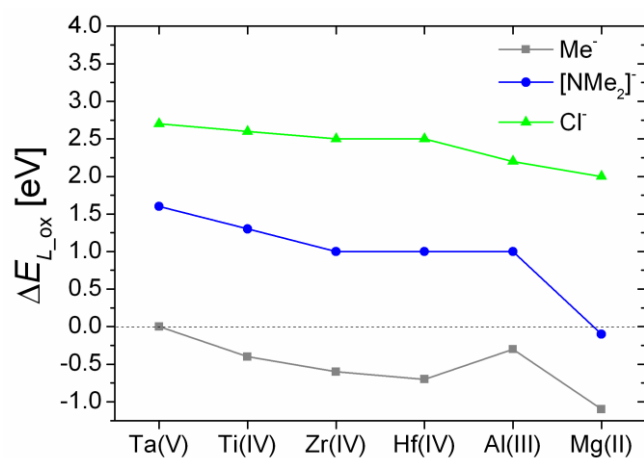
590 Additionally, ligands left on the surface can enhance the clean-up effect by interacting with the substrate  
 591 and this depends on the affinity of the ligand to the substrate and on the chemical character of the  
 592 substrate. We consider first ligand affinity. Metalloid oxides, like  $\text{AsO}_x$ , are susceptible to reduction in  
 593 contact with reducing agents, *e.g.* by the methanide anion  $\text{Me}^-$  in TMA as we showed previously<sup>14</sup> or by  
 594  $\text{CH}_2$  from deprotonated alkylamide (section 3.3.1, C). Self-cleaning by TMA was shown to be governed  
 595 by mobility of the methyl group, which undergoes oxidation, transferring electrons to the surface.  
 596 Various elementary steps were found to be thermodynamically competitive and to lead to a surprising  
 597 range of by-products. However, *dma*  $[\text{NMe}_2]^-$  and chloride  $\text{Cl}^-$  anions are not as strong reducing agents  
 598 as  $\text{Me}^-$ . This is supported by DFT energies, shown in Figure 6, for reactions of transferring those ligands  
 599 from the metal center of the precursor to a surface O site on the  $\text{As}_2\text{O}_3$  substrate. Formation of  $\|\text{O} - L$   
 600 surface intermediates causes reduction of metalloid oxides:



602 In Figure 6 we can see that the chloride ligand, almost independently of which metal center it is bound  
 603 to, is resistant to oxidation with  $\Delta E_{L\_ox}$  around +2.5 eV. The same holds for dma with  $\Delta E_{L\_ox} \approx +1.2$  eV,  
 604 except for  $Mg(NMe_2)_2$  that can dissociate its ligand to the O in the  $As_2O_3$  substrate with  $\Delta E_{L\_ox}$  a little  
 605 below 0 eV. On the contrary, the methyl group is always susceptible to oxidation with exothermic  
 606  $\Delta E_{L\_ox}$  for all metal precursors selected.

607

608 Figure 6. Computed energetics for ligand oxidation at the surface,  $L = [N(Me)_2]^-$ ,  $[Me]^-$ ,  $[Cl]^-$ , and  
 609  $As_2O_3$  reduction according to:  $||As-O|| + \frac{1}{n}ML_n(g) \rightarrow M\frac{1}{n}O\frac{1}{2}(bulk) + ||O-L + ||As-As||$  for  $M = Mg(II)$ ,  
 610  $Al(III)$ ,  $Ti(IV)$ ,  $Zr(IV)$ ,  $Hf(IV)$ ,  $Ta(V)$ . Lines are to guide the eye.



611

612

613 The second factor affecting clean-up is substrate chemistry. If a ligand is susceptible to decomposition,  
 614 specific sites on the surface can activate some bonds of the ligand and this can trigger secondary surface  
 615 reactions that result in clean-up. C-H and N-C bonds of the dma ligand can be activated even at  
 616 relatively low temperature as discussed in previous sections. It has been shown that especially mixed  
 617 nucleophilic-electrophilic character of the surface sites, *e.g.* the zwitterionic character of silicon, affects  
 618 reactivity and transformations of alkylamides<sup>29</sup>. Such reactivity of alkylamides is confirmed by  
 619 experimental observation of formation of Si-H bonds accompanied by the formation of Si-C bonds

620 (leading to incorporation of carbon into the deposited film). Low temperature production of methane has  
621 also been observed, which is evidence for N-C reactivity when depositing oxide films on bare Si or  
622 hydrogen terminated Si substrates. In our calculations, we see similar behaviour of the alkylamide  
623 ligand on the relatively weakly amphoteric  $\text{As}_2\text{O}_3$  substrate. On this oxide substrate H is removed from  
624 the ligand as a proton and formation of O-H bonds is plausible. In this process clean-up is achieved, as  
625 well as producing additional reactive sites (OH) for ALD, but at the same time M-C bonds are formed.  
626 This is because proton elimination causes changes in electronic density on alkylamide carbons: the  $\text{CH}_2$   
627 fragment becomes Lewis basic and this promotes M-C formation (**B**), or the  $\text{CH}_3$  fragment attracts the  
628 charge, and  $\text{CH}_3^-$  detachment is promoted, resulting also in M-C formation (**J**). Some of these reactions  
629 may be more strongly favoured on the mixture of more electropositive  $\text{Ga}^{3+}$  and  $\text{In}^{3+}$  sites of the real III-  
630 V surfaces or even the  $M^{m+}$  sites of the growing film, where bonds tend to be more ionic rather than  
631 covalent. Based on this we can conclude that the above-mentioned mechanisms account for the  
632 reactivity and behaviour of metal alkylamides and can be expected on various substrates featuring Lewis  
633 acid/base sites.

634 An important aspect is whether these processes occur during homodeposition (*i.e.* during the later stages  
635 of growth of *e.g.*  $\text{HfO}_2$  onto  $\text{HfO}_2$ ) and give a CVD component to standard ALD. Clearly during  
636 homodeposition there is no extra driving force from  $M_2\text{O}_n$  formation. On the other hand, decomposition  
637 reactions may be more favoured on the growing film owing to its pronounced nucleophilic-electrophilic  
638 or Lewis acid/base character, as mentioned above. According to our computations, processes yielding  
639 **B-K** are energetically uphill from formation of intermediate **A** onwards. However the formation of **B**  
640 and **J** are only +0.5 eV and +0.8 eV uphill respectively at 0 K for the clean-up process on the  $\text{As}_2\text{O}_3$   
641 substrate and can be expected at elevated temperatures. This finding is supported by experimental  
642 observation of increased efficiency of clean-up with increased temperature. Another aspect is simple  
643 consideration of the strength of the As-O bond and, using the example of  $\text{HfO}_2$ , the Hf-O bond. Clearly  
644 the Hf-O bond, once it is formed, is much stronger and less reactive, which does not favour subsequent

645 CVD reactions. An explicit investigation of CVD reactions on the HfO<sub>2</sub> surface is necessary to fairly  
646 judge the importance of the CVD contribution in case of alkylamide ALD, but is beyond the scope of  
647 this paper.

#### 648 **4. Conclusion**

649 We successfully apply our model for clean-up to explain differences in the performance of various  
650 classes of precursor chemicals in removing native oxide from III-V substrates. Building on the example  
651 of TMA, we identify two separate factors governing the clean-up effect: formation of the metal oxide as  
652 the primary driving force and affinity of the precursor ligand to the III-V oxide substrate as the ancillary  
653 force. That allows an efficient description of interactions of the various precursor ligands with an  
654 oxidised III-V substrate, and of the associated multi-step chemical processes that lead to formation of  
655 the clean-up products. We map out reaction sequences for the alkylamide ligand that lead plausibly to  
656 products that are detected experimentally (aziridine, ethylene, MMI, HCN, methane). Through this  
657 approach, a set of general reactions is generated and comparison is made between several different  
658 precursors, including metal alkylamides Mg[N(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>, Al[N(CH<sub>3</sub>)<sub>2</sub>]<sub>3</sub>, Ti[N(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub>, Zr[N(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub>,  
659 Hf[N(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub>, Ta[N(CH<sub>3</sub>)<sub>2</sub>]<sub>5</sub>; metal methyls: Mg(CH<sub>3</sub>)<sub>2</sub>, Al(CH<sub>3</sub>)<sub>3</sub>, Ti(CH<sub>3</sub>)<sub>4</sub>, Zr(CH<sub>3</sub>)<sub>4</sub>, Hf(CH<sub>3</sub>)<sub>4</sub>,  
660 Ta(CH<sub>3</sub>)<sub>5</sub>; and metal chlorides: MgCl<sub>2</sub>, AlCl<sub>3</sub>, TiCl<sub>4</sub>, ZrCl<sub>4</sub>, HfCl<sub>4</sub>, TaCl<sub>5</sub>. We can therefore predict the  
661 best reagent for achieving the clean-up effect.

662 We predict that the investigated methyl precursors are the best reagents for deposition of dielectrics and  
663 performing clean-up. Unfortunately, most of them are very unstable compounds. Clean-up is most  
664 effective when depositing MgO, as Mg<sup>2+</sup> works as the most effective scavenger of O<sup>2-</sup>. Clean-up with  
665 metal chlorides seems to have a fundamentally different mechanism, probably involving removal of the  
666 O from the native oxide film and passivation with Cl groups.

667 The first principles study shows that clean-up with metal alkylamides has a similar mechanism to clean-  
668 up with metal methyls as regards the scavenging of oxygen from weak As, Ga and In oxides. Arising  
669 from this, ligand exchange can in principle lead to a clean-up product: tris(dimethylamino)arsine.

670 However steric hindrance and the bulky character of the alkylamide ligand are rate limiting factors,  
671 which in this case are very pronounced and suggest that this particular reaction will not proceed.

672 Our study also shows the difference in mechanism underlying the consumption of III-V oxides with  
673 alkylamido precursors from the one taking place with TMA. In the case of the alkylamide ligand,  
674 thermal decomposition rather than migration of the entire ligand on the oxide surface is dominant,  
675 taking into account the bulky character of the ligand and its known reactivity in contact with a  
676 semiconductor or metallic surface. Clean-up of the reducible As oxide substrate is therefore enhanced  
677 by secondary decomposition surface reactions, not by oxidation of the entire alkylamide. The H  
678 elimination process that forms hydroxyl groups and As-C bound species (**B**) is exothermic or neutral at  
679 0 K and kinetically demanding. The migration of these decomposition intermediates from an As site to  
680 an O site (**C**) and direct reduction of the substrate is only slightly endothermic. Successive  
681 dehydrogenation though becomes progressively less favored. Instead, the first H elimination may be  
682 followed by another plausible reaction – N-C bond scission (**J**), which can lead to low temperature  
683 methane production, albeit without the clean-up effect. Thermal activation is needed for formation and  
684 desorption of products that arise from these decomposition structures: most likely N-  
685 methylmethyleimine and aziridine, possibly along with methane, ethylene and dinitrogen. A specific  
686 requirement of the substrate is that it contain both Lewis acid and Lewis base sites, which can activate  
687 secondary surface reactions of ligands that are susceptible to decomposition, like the dimethylamido  
688 group. These redox processes do lead to the reduction of arsenic oxides to metallic arsenic, which in  
689 turn can reduce gallium and indium oxides to pure III-V material. Some of the reactions that we have  
690 presented therefore account for the clean-up effect, but they occur in parallel with reactions that do not  
691 achieve clean-up.

692 More generally we show that organometallic reagents react readily with substrates featuring less  
693 electropositive metals. In presence of metals like Si, As, Ga and In, a reactive polar metal-organic ligand  
694 bond, *e.g.* Al-C, is broken and formation of more covalent bond, *e.g.* As-C, is favoured. These reactions



695 might be possible during homodeposition and can thereby give a CVD component to standard ALD, as  
696 is well-documented for alkylamides. The mechanisms described here are in line with observations on Si  
697 surfaces as well. The same mechanisms can therefore be expected on other substrates, such as oxides  
698 and nitrides, that show a mix of Lewis acid/base sites.

699

## 700 ASSOCIATED CONTENT

701 **Supporting Information Available:** lattice parameters and space groups, along with *k*-point  
702 sampling for optimised bulk structures; geometrical parameters for optimised gaseous molecules;  
703 additional list of possible clean-up *intermediates* that are formed during ALD III-V substrate exposure  
704 to alkylamide metal precursors – energetics for the interaction of dma ligand with the substrate ( $\Delta E_L$ );  
705 surface models showing products of the dissociative adsorption of Hf[N(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub> precursor; reaction  
706 profile for dissociative adsorption of Hf[N(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub> precursor; energetics for ligand exchange between  
707 precursor metal centre and bulk III-V oxide: As<sub>2</sub>O<sub>3</sub>, As<sub>2</sub>O<sub>5</sub>, Ga<sub>2</sub>O<sub>3</sub> and In<sub>2</sub>O<sub>3</sub> for  $L = [\text{Me}]^-$ ;  $[\text{Cl}]^-$ .

708 This material is available free of charge via the Internet at <http://pubs.acs.org>.

709

## 710 AUTHOR INFORMATION

### 711 Corresponding author

712 \*E-mail address: [simon.elliott@tyndall.ie](mailto:simon.elliott@tyndall.ie).

### 713 Notes

714 The authors declare no competing financial interest.

715

716

717

718 ACKNOWLEDGMENT

719 This work was funded by Science Foundation Ireland under grant no. 07/SRC/I1172 (“FORME”,  
720 [www.tyndall.ie/forme](http://www.tyndall.ie/forme)). The authors wish to acknowledge the SFI/HEA Irish Centre for High-End  
721 Computing (ICHEC) for the provision of computational facilities and support.

722

723 REFERENCES

- 724 1. Miikkulainen, V.; Leskela, M.; Ritala, M.; Puurunen, R. L., Crystallinity of inorganic films  
725 grown by atomic layer deposition: Overview and general trends. *Journal of Applied Physics* **2013**, *113*  
726 (2), 021301-101.
- 727 2. Huang, M. L.; Chang, Y. C.; Chang, C. H.; Lee, Y. J.; Chang, P.; Kwo, J.; Wu, T. B.; Hong, M.,  
728 Surface passivation of III-V compound semiconductors using atomic-layer-deposition-grown Al<sub>2</sub>O<sub>3</sub>.  
729 *Applied Physics Letters* **2005**, *87* (25), 252104-3.
- 730 3. (a) Chang, C. H.; Chiou, Y. K.; Chang, Y. C.; Lee, K. Y.; Lin, T. D.; Wu, T. B.; Hong, M.;  
731 Kwo, J., Interfacial self-cleaning in atomic layer deposition of HfO<sub>2</sub> gate dielectric on In<sub>0.15</sub>Ga<sub>0.85</sub>As.  
732 *Applied Physics Letters* **2006**, *89* (24), 242911-3; (b) Delabie, A.; Brunco, D. P.; Conard, T.; Favia, P.;  
733 Bender, H.; Franquet, A.; Sioncke, S.; Vandervorst, W.; Van Elshocht, S.; Heyns, M.; Meuris, M.; Kim,  
734 E.; McIntyre, P. C.; Saraswat, K. C.; LeBeau, J. M.; Cagnon, J.; Stemmer, S.; Tsai, W., Atomic Layer  
735 Deposition of Hafnium Oxide on Ge and GaAs Substrates: Precursors and Surface Preparation. *Journal*  
736 *of The Electrochemical Society* **2008**, *155* (12), H937-H944.
- 737 4. (a) Granados-Alpizar, B.; Muscat, A. J., Surface reactions of TiCl<sub>4</sub> and Al(CH<sub>3</sub>)<sub>3</sub> on GaAs(100)  
738 during the first half-cycle of atomic layer deposition. *Surface Science* **2011**, *605* (13-14), 1243-1248; (b)  
739 Gougousi, T.; Lacia, J. W., Native oxide consumption during the atomic layer deposition of TiO<sub>2</sub> films  
740 on GaAs (100) surfaces. *Thin Solid Films* **2010**, *518* (8), 2006-2009.

- 741 5. Gougousi, T.; Ye, L., Interface Between Atomic Layer Deposition Ta<sub>2</sub>O<sub>5</sub> Films and GaAs(100)  
742 Surfaces. *The Journal of Physical Chemistry C* **2012**, *116* (16), 8924-8931.
- 743 6. (a) Tallarida, M.; Adelman, C.; Delabie, A.; Van Elshocht, S.; Caymax, M.; Schmeisser, D.,  
744 Surface chemistry and Fermi level movement during the self-cleaning of GaAs by trimethyl-aluminum.  
745 *Applied Physics Letters* **2011**, *99* (4), 042906; (b) Lin, L.; Robertson, J., Defect states at III-V  
746 semiconductor oxide interfaces. *Appl. Phys. Lett.* **2011**, *98* (8), 082903.
- 747 7. (a) O'Mahony, A.; Monaghan, S.; Chiodo, R.; Povey, I.; Cherkaoui, K.; Nagle, R.; O'Connor, E.;  
748 Long, R.; Djara, V.; O'Connell, D.; Crupi, F.; Pemble, M.; Hurley, P. K., Structural and Electrical  
749 Analysis of Thin Interface Control Layers of MgO or Al<sub>2</sub>O<sub>3</sub> Deposited by Atomic Layer Deposition and  
750 Incorporated at the High-k/III-V Interface of MO<sub>2</sub>/In<sub>x</sub>Ga<sub>1-x</sub>As (M = Hf|Zr, x = 0|0.53) Gate Stacks. *ECS*  
751 *Transactions* **2010**, *33* (2), 69-82; (b) O'Mahony, A.; Monaghan, S.; Provenzano, G.; Povey, I. M.;  
752 Nolan, M. G.; O'Connor, E.; Cherkaoui, K.; Newcomb, S. B.; Crupi, F.; Hurley, P. K.; Pemble, M. E.,  
753 Structural and electrical analysis of the atomic layer deposition of HfO<sub>2</sub>/n-In<sub>0.53</sub>Ga<sub>0.47</sub>As capacitors with  
754 and without an Al<sub>2</sub>O<sub>3</sub> interface control layer. *Applied Physics Letters* **2010**, *97* (5), 052904-3; (c)  
755 O'Connor, E.; Brennan, B.; Djara, V.; Cherkaoui, K.; Monaghan, S.; Newcomb, S. B.; Contreras, R.;  
756 Milojevic, M.; Hughes, G.; Pemble, M. E.; Wallace, R. M.; Hurley, P. K., A systematic study of  
757 (NH<sub>4</sub>)<sub>2</sub>S passivation (22%, 10%, 5%, or 1%) on the interface properties of the Al<sub>2</sub>O<sub>3</sub>/In<sub>0.53</sub>Ga<sub>0.47</sub>As/InP  
758 system for n-type and p-type In<sub>0.53</sub>Ga<sub>0.47</sub>As epitaxial layers. *Journal of Applied Physics* **2011**, *109* (2),  
759 024101-10; (d) Monaghan, S.; O'Mahony, A.; Cherkaoui, K.; O'Connor, E.; Povey, I. M.; Nolan, M. G.;  
760 O'Connell, D.; Pemble, M. E.; Hurley, P. K.; Provenzano, G.; Crupi, F.; Newcomb, S. B. In *Electrical*  
761 *analysis of three-stage passivated In<sub>0.53</sub>Ga<sub>0.47</sub>As capacitors with varying HfO<sub>2</sub> thicknesses and*  
762 *incorporating an Al<sub>2</sub>O<sub>3</sub> interface control layer*, AVS: 2011; pp 01A807-8.
- 763 8. Hinkle, C. L.; Sonnet, A. M.; Vogel, E. M.; McDonnell, S.; Hughes, G. J.; Milojevic, M.; Lee,  
764 B.; Aguirre-Tostado, F. S.; Choi, K. J.; Kim, H. C.; Kim, J.; Wallace, R. M., GaAs interfacial self-  
765 cleaning by atomic layer deposition. *Applied Physics Letters* **2008**, *92* (7), 071901-3.

- 766 9. Gougousi, T.; Hackley, J. C.; Demaree, J. D.; Lacin, J. W., Growth and Interface Evolution of  
767 HfO<sub>2</sub> Films on GaAs(100) Surfaces. *Journal of The Electrochemical Society* **2010**, *157* (5), H551-H556.
- 768 10. Frank, M. M.; Wilk, G. D.; Starodub, D.; Gustafsson, T.; Garfunkel, E.; Chabal, Y. J.; Grazul, J.;  
769 Muller, D. A., HfO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> gate dielectrics on GaAs grown by atomic layer deposition. *Applied*  
770 *Physics Letters* **2005**, *86* (15), 152904-3.
- 771 11. Milojevic, M.; Aguirre-Tostado, F. S.; Hinkle, C. L.; Kim, H. C.; Vogel, E. M.; Kim, J.;  
772 Wallace, R. M., Half-cycle atomic layer deposition reaction studies of Al<sub>2</sub>O<sub>3</sub> on In<sub>0.2</sub>Ga<sub>0.8</sub>As (100)  
773 surfaces. *Applied Physics Letters* **2008**, *93* (20), 202902-3.
- 774 12. Elliott, S. D., Atomic-scale simulation of ALD chemistry. *Semiconductor Science and*  
775 *Technology* **2012**, *27* (7), 074008.
- 776 13. Hegde, G.; Klimeck, G.; Strachan, A., Role of surface orientation on atomic layer deposited  
777 Al<sub>2</sub>O<sub>3</sub>/GaAs interface structure and Fermi level pinning: A density functional theory study. *Applied*  
778 *Physics Letters* **2011**, *99* (9), 093508-3.
- 779 14. Klejna, S.; Elliott, S. D., First-Principles Modeling of the “Clean-Up” of Native Oxides during  
780 Atomic Layer Deposition onto III–V Substrates. *The Journal of Physical Chemistry C* **2012**, *116* (1),  
781 643-654.
- 782 15. Kresse, G.; Furthmüller, J., Efficient iterative schemes for ab initio total-energy calculations  
783 using a plane-wave basis set. *Physical Review B* **1996**, *54* (16), 11169.
- 784 16. Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.;  
785 Fiolhais, C., Atoms, molecules, solids, and surfaces: Applications of the generalized gradient  
786 approximation for exchange and correlation. *Physical Review B* **1992**, *46* (11), 6671.
- 787 17. (a) Vanderbilt, D., Soft self-consistent pseudopotentials in a generalized eigenvalue formalism.  
788 *Physical Review B* **1990**, *41* (11), 7892; (b) Kresse, G.; Hafner, J., Norm-conserving and ultrasoft  
789 pseudopotentials for first-row and transition elements. *Journal of Physics: Condensed Matter* **1994**, *6*  
790 (40), 8245.

- 791 18. Wyckoff, R. W. G., Crystal Structures. *Crystal Structures* **Wiley Interscience, New York,**  
792 **1963.**
- 793 19. Ballirano, P.; Maras, A. Z., Refinement of the crystal structure of arsenolite, As<sub>2</sub>O<sub>3</sub>. *Kristallogr.-*  
794 *New Cryst. Struct.* **2002**, *217*, 177-178.
- 795 20. Henkelman, G.; Arnaldsson, A.; Jónsson, H., A fast and robust algorithm for Bader  
796 decomposition of charge density. *Computational Materials Science* **2006**, *36* (3), 354-360.
- 797 21. Henkelman, G.; Uberuaga, B. P.; Jonsson, H., A climbing image nudged elastic band method for  
798 finding saddle points and minimum energy paths. *The Journal of Chemical Physics* **2000**, *113* (22),  
799 9901-9904.
- 800 22. (a) Murray, C.; Elliott, S. D., Density Functional Theory Predictions of the Composition of  
801 Atomic Layer Deposition-Grown Ternary Oxides. *ACS Applied Materials & Interfaces* **2013**, *5* (9),  
802 3704-3715; (b) Elliott, S. D., Improving ALD growth rate via ligand basicity: Quantum chemical  
803 calculations on lanthanum precursors. *Surface and Coatings Technology* **2007**, *201* (22–23), 9076-9081.
- 804 23. Suri, R.; Lichtenwalner, D. J.; Misra, V., Interfacial self cleaning during atomic layer deposition  
805 and annealing of HfO<sub>2</sub> films on native (100)-GaAs substrates. *Applied Physics Letters* **2010**, *96* (11),  
806 112905-3.
- 807 24. Lamagna, L.; Wiemer, C.; Perego, M.; Spiga, S.; Rodríguez, J.; Santiago Coll, D.; Grillo, M. E.;  
808 Klejna, S.; Elliott, S. D., Mechanisms for Substrate-Enhanced Growth during the Early Stages of  
809 Atomic Layer Deposition of Alumina onto Silicon Nitride Surfaces. *Chemistry of Materials* **2012**, *24*  
810 (6), 1080-1090.
- 811 25. (a) Marx, D.; Asahi, H.; Liu, X. F.; Higashiwaki, M.; Villaflor, A. B.; Miki, K.; Yamamoto, K.;  
812 Gonda, S.; Shimomura, S.; Hiyamizu, S., Low temperature etching of GaAs substrates and improved  
813 morphology of GaAs grown by metalorganic molecular beam epitaxy using trisdimethylaminoarsenic  
814 and triethylgallium. *Journal of Crystal Growth* **1995**, *150*, Part 1 (0), 551-556; (b) Salim, S.; Ping Lu,  
815 J.; Jensen, K. F.; Bohling, D. A., Surface reactions of dimethylaminoarsine during MOMBE of GaAs.  
816 *Journal of Crystal Growth* **1992**, *124* (1–4), 16-22; (c) Shi, B.; Tu, C., A kinetic model for

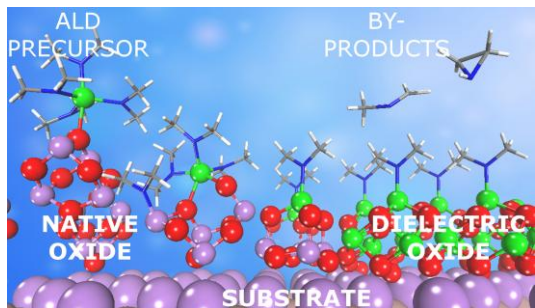
- 817 tris(dimethylamino) arsine decomposition on GaAs(100) surfaces. *Journal of Electronic Materials*  
818 **1999**, 28 (1), 43-49.
- 819 26. Puurunen, R. L., Formation of Metal Oxide Particles in Atomic Layer Deposition During the  
820 Chemisorption of Metal Chlorides: A Review. *Chemical Vapor Deposition* **2005**, 11 (2), 79-90.
- 821 27. Kim, T.; Zaera, F., Surface Chemistry of Pentakis(dimethylamido)tantalum on Ta Surfaces. *The*  
822 *Journal of Physical Chemistry C* **2011**, 115 (16), 8240-8247.
- 823 28. Li, K.; Li, S.; Li, N.; Dixon, D. A.; Klein, T. M., Tetrakis(dimethylamido)hafnium Adsorption  
824 and Reaction on Hydrogen Terminated Si(100) Surfaces. *The Journal of Physical Chemistry C* **2010**,  
825 *114* (33), 14061-14075.
- 826 29. (a) Rodríguez-Reyes, J. C., Mechanisms of adsorption and decomposition of metal alkylamide  
827 precursors for ultrathin film growth. *J. Appl. Phys.* **2008**, 104 (8), 084907; (b) Rodríguez-Reyes, J. C.  
828 F.; Teplyakov, A. V., Chemisorption of Tetrakis(dimethylamido)titanium on Si(100)-2 × 1: C–H and  
829 C–N Bond Reactivity Leading to Low-Temperature Decomposition Pathways. *The Journal of Physical*  
830 *Chemistry C* **2008**, 112 (26), 9695-9705.
- 831 30. (a) Bradley, D. C.; Chisholm, M. H., Transition-metal dialkylamides and disilylamides.  
832 *Accounts of Chemical Research* **1976**, 9 (7), 273-280; (b) Salim, S.; Lim, C. K.; Jensen, K. F., Gas-  
833 Phase Decomposition Reactions of Tris(dimethylamino)phosphine, -Arsine, and -Stibine Reagents.  
834 *Chemistry of Materials* **1995**, 7 (3), 507-516.
- 835 31. Ando, T., Ultimate Scaling of High-κ Gate Dielectrics: Higher-κ or Interfacial Layer  
836 Scavenging? *Materials* **2012**, 5 (3), 478-500.

837

838

839

840 TABLE OF CONTENTS (TOC)



841

842 Deleterious native oxides of semiconductor substrate are transformed into dielectric oxide when atomic  
843 layer deposition technique (ALD) with the appropriate precursor chemical is used during transistor  
844 fabrication.

845