Removal Reaction Mechanisms During Thermal Atomic Layer Etching of Aluminum Oxide: A First-Principles Study
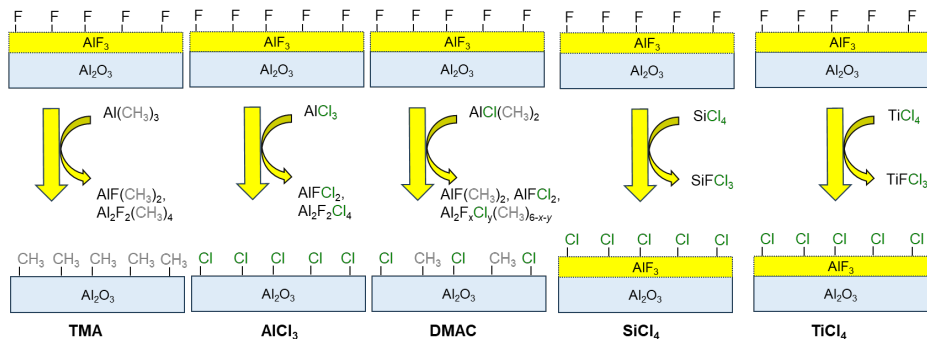
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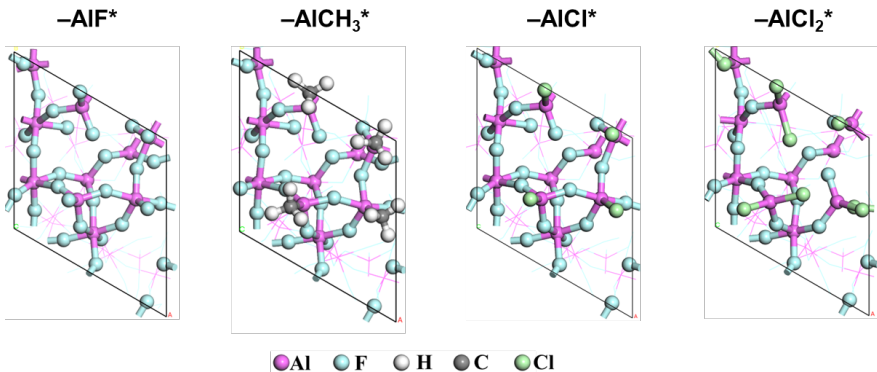[1]Department of Nanotechnology and Advanced Materials Engineering, Sejong University, Seoul Republic of Korea
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Summary – Reaction Mechanisms

TMA $AlCl_3$ DMAC $SiCl_4$ $TiCl_4$

Amorphous AlF_3 slab models used in this study

–AlF*   –AlCH_3*   –AlCl*   –AlCl_2*

Al   F   H   C   Cl

Simulation of Removal Reactions

Precursor	Step	Reactions	E_A	ΔG
$Al(CH_3)_3$	1	$(AlF)_3AlF* + Al(CH_3)_3 \rightarrow (AlF)_3AlCH_3* + AlF(CH_3)_3$	0.23	-0.87
	2	$(AlF)_3AlCH_3* + Al(CH_3)_3 \rightarrow -Al + -Al_2F + Al_2F_2(CH_3)_4$	1.08	-0.85
$AlCl_3$	1	$(AlF)_3AlF* + AlCl_3 \rightarrow (AlF)_3AlCl* + AlF(CH_3)_3$	1.00	-0.19
	2	$(AlF)_3AlCl* + AlCl_3 \rightarrow -Al + -Al_2F + Al_2F_2Cl_4$	0.84	-0.51
$AlCl(CH_3)_2$	1a	$(AlF)_3AlF* + AlCl(CH_3)_2 \rightarrow (AlF)_3AlCH_3* + AlFClCH_3$	0.17	-0.57
	1b	$(AlF)_3AlF* + AlCl(CH_3)_2 \rightarrow (AlF)_3AlCl* + AlF(CH_3)_2$	0.15	-0.16
	2a	$(AlF)_3AlCH_3* + AlCl(CH_3)_2 \rightarrow -Al + -Al_2F + Al_2F_2Cl(CH_3)_2$	0.74	-0.32
	2b	$(AlF)_3AlCl* + AlCl(CH_3)_2 \rightarrow -Al + -Al_2F + Al_2FCl_2(CH_3)_2$	0.54	-0.24
$SiCl_4$	1	1. $(AlF)_3AlF* + SiCl_4 \rightarrow (AlF)_3AlCl* + SiFCl_3$	0.74	-0.42
		2. $(AlF)_3AlCl* \rightarrow -Al + -Al_2F + AlF_2Cl$	1.63	0.15
	2	1. $(AlF)_3AlCl* + SiCl_4 \rightarrow (AlF)_2(AlCl)AlCl* + SiFCl_3$	1.06	-0.41
		2. $(AlF)_2(AlCl)AlCl* \rightarrow -Al + -Al_2F + AlFCl_2$	1.62	0.17
	3	1. $(AlF)_2(AlCl)AlCl* + SiCl_4 \rightarrow (AlF)(AlCl)_2AlCl* + SiFCl_3$	1.42	0.29
		2. $(AlF)(AlCl)_2AlCl* \rightarrow -Al + -Al_2F + AlCl_3$	0.77	-0.62
$TiCl_4$	1	1. $(AlF)_3AlF* + TiCl_4 \rightarrow (AlF)_3AlCl* + TiFCl_3$	0.51	-0.14
		2. $(AlF)_3AlCl* \rightarrow -Al + -Al_2F + AlF_2Cl$	1.63	0.15
	2	1. $(AlF)_3AlCl* + TiCl_4 \rightarrow (AlF)_2(AlCl)AlCl* + TiFCl_3$	0.25	-0.12
		2. $(AlF)_2(AlCl)AlCl* \rightarrow -Al + -Al_2F + AlFCl_2$	1.62	0.17
	3	1. $(AlF)_2(AlCl)AlCl* + TiCl_4 \rightarrow (AlF)(AlCl)_2AlCl* + TiFCl_3$	0.97	0.66
		2. $(AlF)(AlCl)_2AlCl* \rightarrow -Al + -Al_2F + AlCl_3$	0.77	-0.62