# Supporting Information

## Unveiling surface reactivity: the crucial role of auxiliary ligands in Gallium amidinate-based precursors for Atomic Layer Deposition

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# 1. General procedures

All air and moisture sensitive reactions were performed under inert atmosphere using a vacuum line, inert Schlenk techniques ($N_2$) and a glove box (Ar, <0.1 ppm $H_2O$, <0.1 ppm $O_2$) with oven-dried glassware unless other notified. Reagents were used as received from commercially available suppliers without further purification unless otherwise noticed. $CH_2Cl_2$, pentane, and toluene were taken from solvent purification system (MBraun-SPS). THF, $^{i}$PrOH, and $Et_2O$ were distilled over Na and degassed using freeze-pump technique. NMR spectra were recorded on a Bruker AC-300 SY spectrometer at 300 MHz for $^{1}$H, 120 MHz for $^{31}$P and 75 MHz for $^{13}$C. Solvent peaks were used as internal references for $^{1}$H and $^{13}$C chemical shifts (ppm). $^{31}P\{^{1}H\}$ NMR spectra are relative to an 85% $H_3PO_4$ external reference. Unless otherwise mentioned, NMR spectra were recorded at 300 K. The spectra were analysed with Topspin software.

Mass spectrometry experiments were performed on a Tims-TOF mass spectrometer (Bruker, France) equipped with atmospheric pressure chemical ionization (APCI) source with one direct probe to introduce solid compounds. Few μg of sample were deposit into glass capillary. All mass spectra were produced in positive mode. Capillary and end plate voltages were set at 4.2 kV and 0.5 kV for experiments, Corona for APCI was set at 4000nA. Nitrogen was used as the nebuliser and drying gas at 3 bar and 2 L $min^{-1}$, respectively, with a drying temperature of 250 °C. APCI heater was set at 300°C. Tuning mix (Agilent, France) was used for calibration. The elemental compositions of all ions were determined with the instrument software Data Analysis, the precision of mass measurement was less than 5 ppm.

X-ray crystallography data were collected at 150 K on a Bruker Kappa APEX II diffractometer using a Mo-κ (λ = 0.71069Å) X-ray source and a graphite monochromator. The crystal structures were solved using Shelxt33[1] or olex[2] and refined using Shelxl-97 or Shelxl-2014.[1] ORTEP drawings were made using ORTEP III[3] for Windows. Details of crystal data Details of crystal data and structure refinements are summarized in Table S1.

# 2. Molecular compound characterisation

## 2.1. $^{1}H$ and $^{13}C$ NMR spectra of LLi, $LGaCl_2$, $LGaMe_2$ and $LGa(NMe_2)_2$ with L = N,N'-di-tertbutylacetamidinato

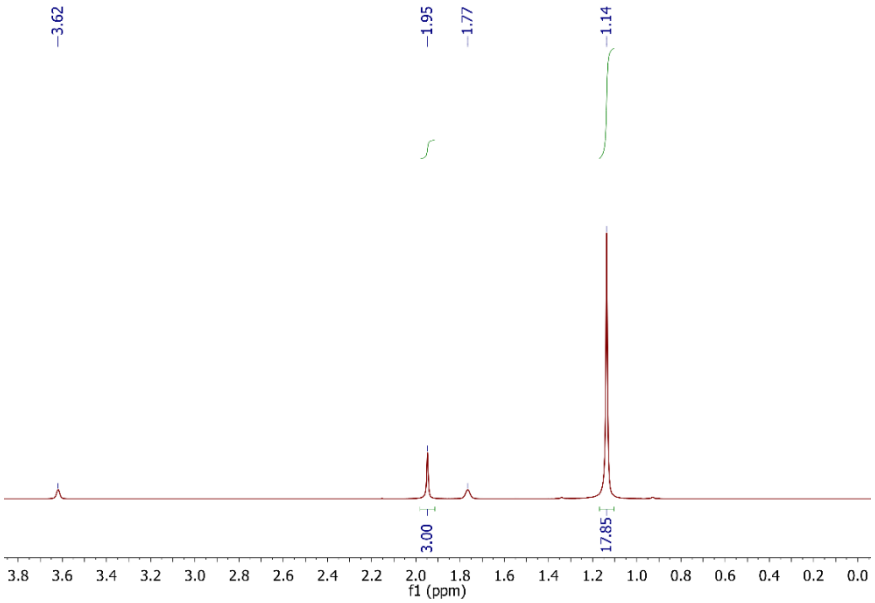



Figure S1: $^{1}H$-NMR of **LLi** in THF-$d_8$, 300 MHz.

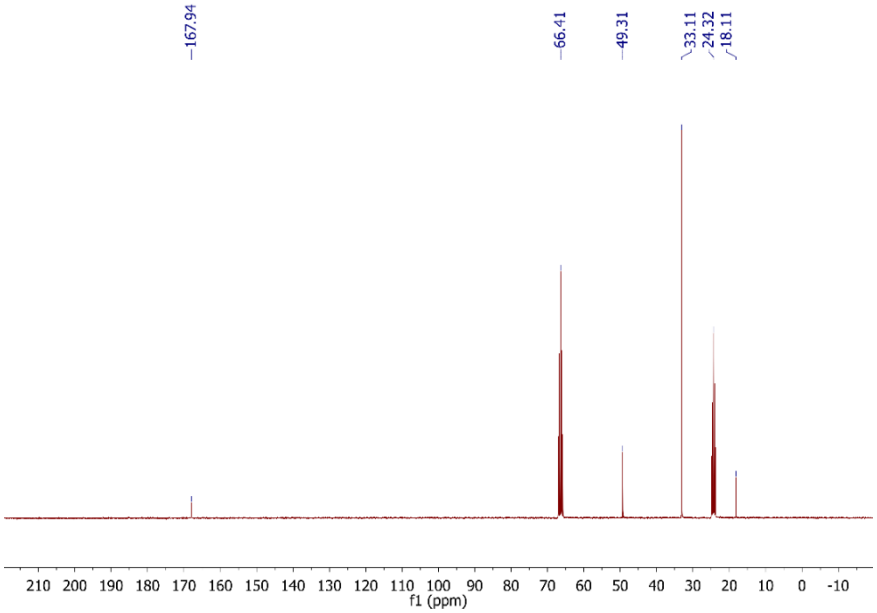



Figure S2: $^{13}C$-NMR of **LLi** in THF-$d_8$, 300 MHz.

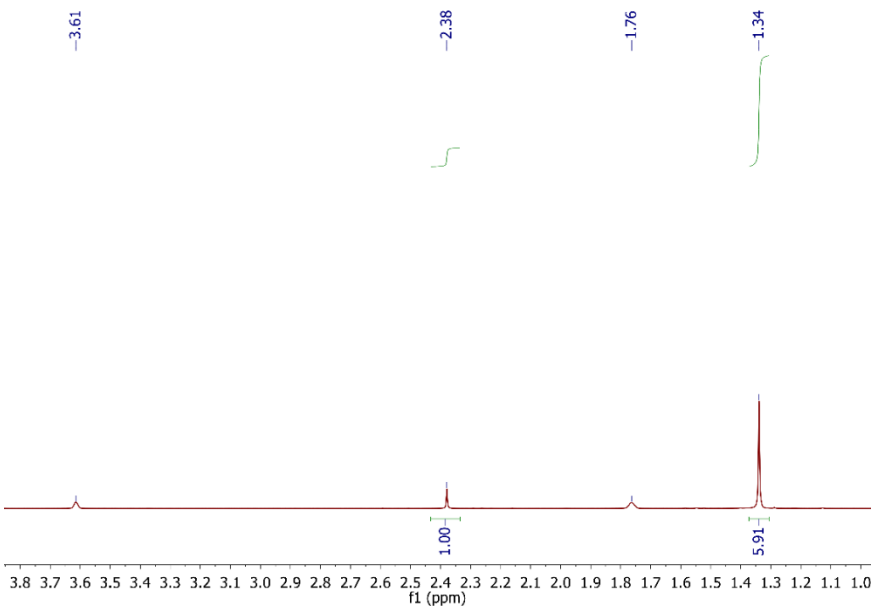



Figure S3: $^{1}$H-NMR of **$LGaCl_2$** in THF-$d_8$, 300 MHz.

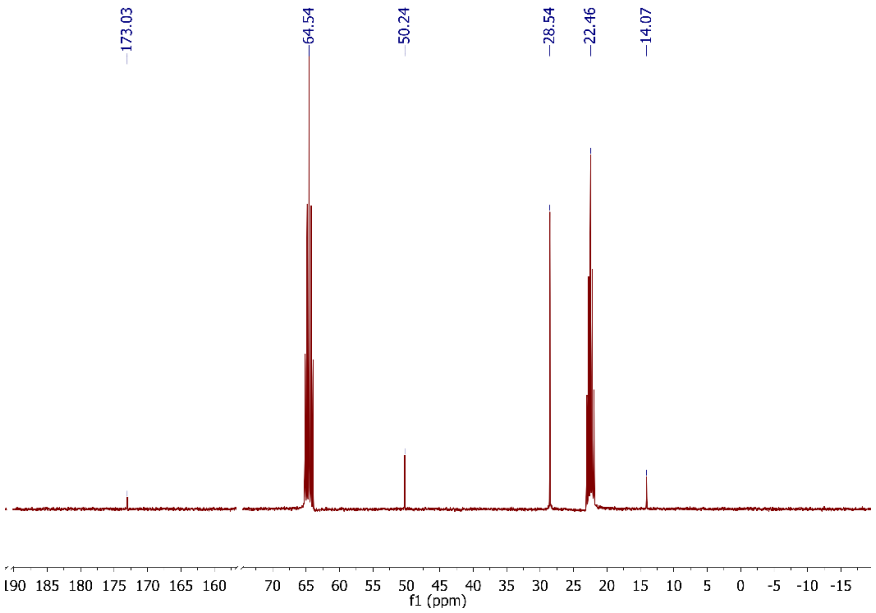



Figure S4: $^{13}$C-NMR of **$LGaCl_2$** in THF-$d_8$, 300 MHz.

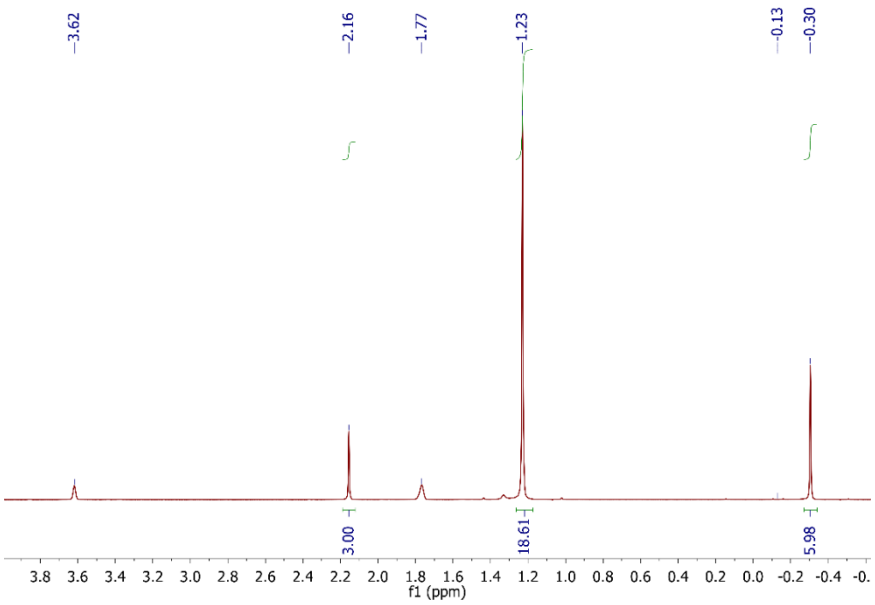



Figure S5: $^{1}$H-NMR of **LGaMe$_2$** in THF-d$_8$, 300 MHz.

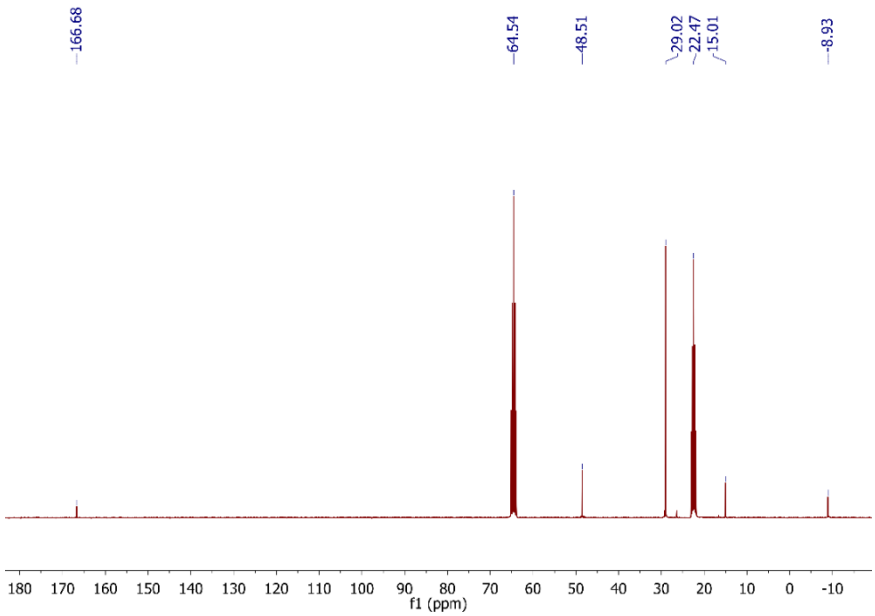



Figure S6: $^{13}$C-NMR of **LGaMe$_2$** in THF-d$_8$, 300 MHz.

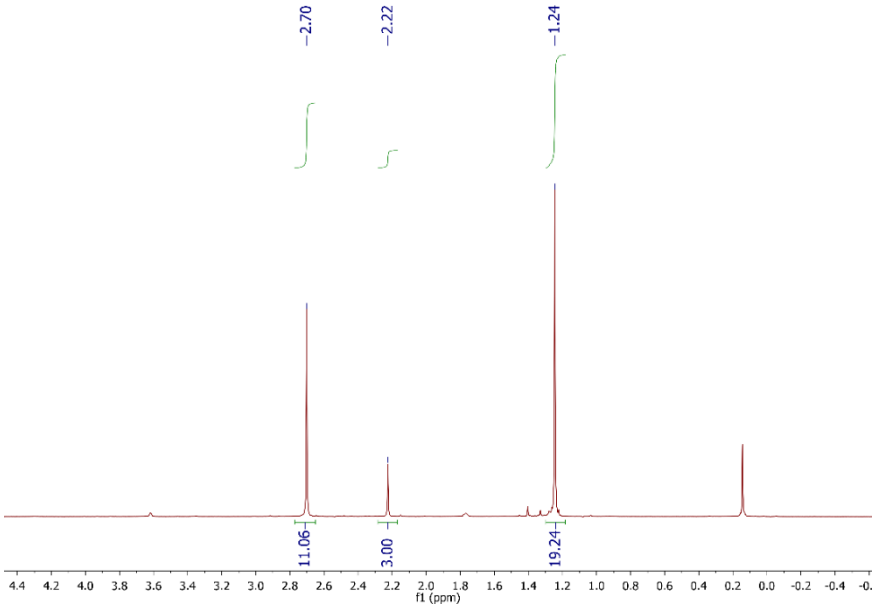



Figure S8: $^{1}$H-NMR of **LGa(NMe$_2$)$_2$** in THF-d$_8$, 300 MHz.

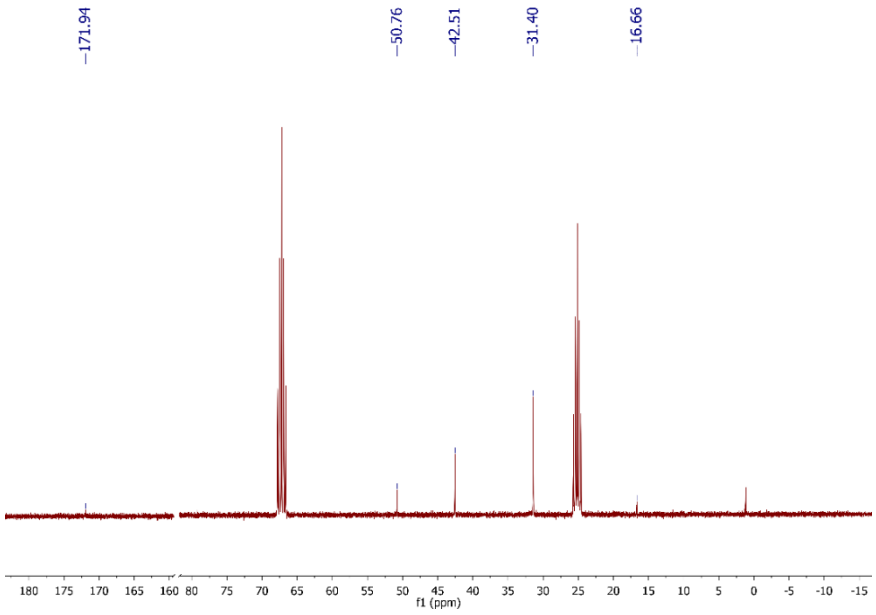



Figure S7: $^{13}$C-NMR of **LGa(NMe$_2$)$_2$** in THF-d$_8$, 300 MHz.

## 2.2. X-ray Diffraction data

Table S1: Crystal data and structure refinement of **LLi** and **$LGaCl_2$** with L = N,N'-di-*tert*butylacetamidinato

| Compound | **LLi** | **$LGaCl_2$** |
|---|---|---|
| Empirical formula | $C_{15}H_{31.5}Li_{1.5}N_3$ | $C_{10}H_{21}Cl_2GaN_2$ |
| Formula weight | 264.34 | 309.91 |
| Temperature/K | 149.99 | 150.0 |
| Crystal system | monoclinic | monoclinic |
| Space group | $C_{2/c}$ | $P2_1/n$ |
| a/Å | 16.5502(14) | 8.1083(10) |
| b/Å | 11.7796(10) | 11.6422(13) |
| c/Å | 19.403(2) | 15.6810(18) |
| α/° | 90 | 90 |
| β/° | 114.049(3) | 96.471(4) |
| γ/° | 90 | 90 |
| Volume/Å$^3$ | 3454.3(6) | 1470.8(3) |
| Z | 8 | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.017 | 1.400 |
| μ/mm$^{-1}$ | 0.059 | 2.209 |
| F(000) | 1176 | 640.0 |
| Crystal size/mm$^3$ | 0.32 × 0.20 × 0.16 | 0.36 × 0.14 × 0.08 |
| Radiation | MoKα (λ = 0.71073) | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 4.42 to 48.32 | 5.228 to 58.256 |
| Index ranges | -20 ≤ h ≤ 13, -14 ≤ k ≤ 14, -23 ≤ l ≤ 24 | -11 ≤ h ≤ 10, -15 ≤ k ≤ 15, -21 ≤ l ≤ 21 |
| Reflections collected | 23662 | 22842 |
| Independent reflections | 3662 [$R_{int}$ = 0.0607, $R_{sigma}$ = 0.0423] | 3948 [$R_{int}$ = 0.0795, $R_{sigma}$ = 0.0552] |
| Data/restraints/parameters | 3662/3/202 | 3948/0/143 |
| Goodness-of-fit on $F^2$ | 1.031 | 1.016 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0528, w$R_2$ = 0.1318 | $R_1$ = 0.0349, w$R_2$ = 0.0731 |
| Final R indexes [all data] | $R_1$ = 0.0804, w$R_2$ = 0.1503 | $R_1$ = 0.0577, w$R_2$ = 0.0840 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.44/-0.22 | 0.46/-0.53 |
| CCDC number | 2409944 | 2409945 |

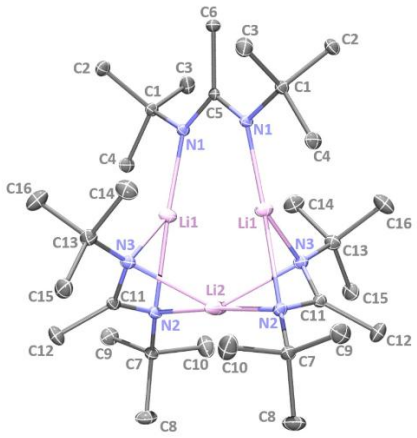



Figure S9: X-ray structure of **LLi** (with thermal ellipsoids drawn at the 20% probability level). The H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Li1-N1= 1.960(3); Li1-N3= 2.000(3); Li1-N2= 2.223(3); Li2-N2= 1.9624(14); Li2-N3= 2.321(3); N1-C5= 1.3337(17); N2-C11= 1.348(2); N3-C11= 1.332(2); N1-C5-N1= 117.02(19); N3-C11-N2= 112.15(14); N1-Li1-N2= 168.55(19); N1-Li1-N3= 127.93(18); Li1-N2-Li2= 74.11(16); Li1-N3-Li2= 71.26(13).

# 3. Quartz Crystal Microbalance (QCM) data

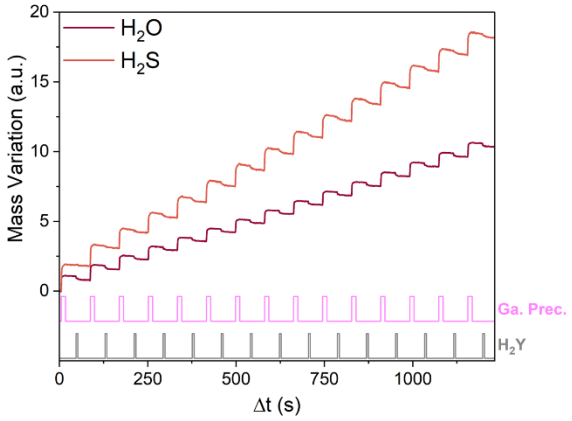



Figure S10: Mass variations measured by *in situ* QCM measurements during ALD of $GaO_x$ (red) and $GaS_x$ (orange) at $T_{dep}$ = 150°C using **TDMAG** as gallium precursor. The lower part of the graphs indicates the pulse sequence.

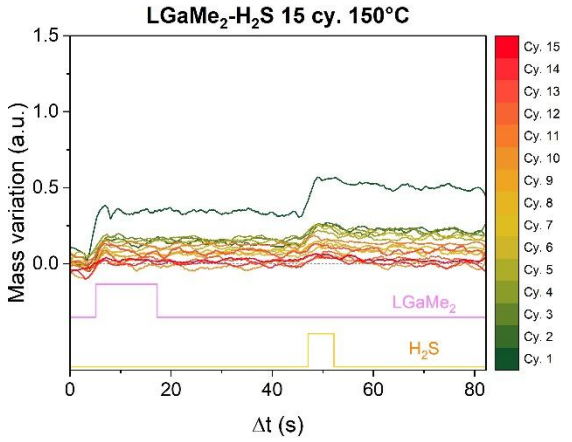



Figure S11: Overlay of consecutive cycles of ALD of $GaS_x$ measured by in situ QCM using **$LGaMe_2$** as gallium precursor. Green traces indicate initial cycles and red traces the last ones (15 total cycles).

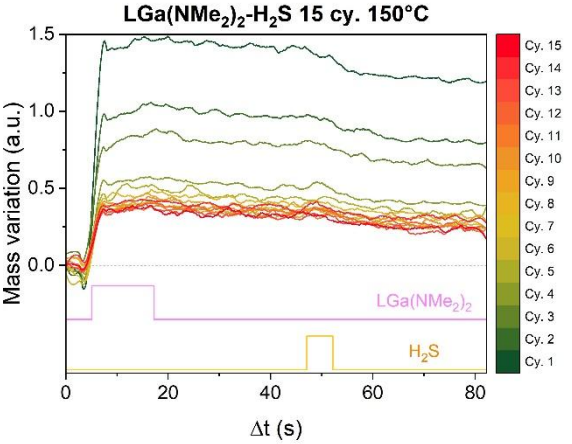



Figure S12: Overlay of consecutive cycles of ALD of $GaS_x$ measured by in situ QCM using **$LGa(NMe_2)_2$** as gallium precursor. Green traces indicate initial cycles and red traces the last ones (15 total cycles).

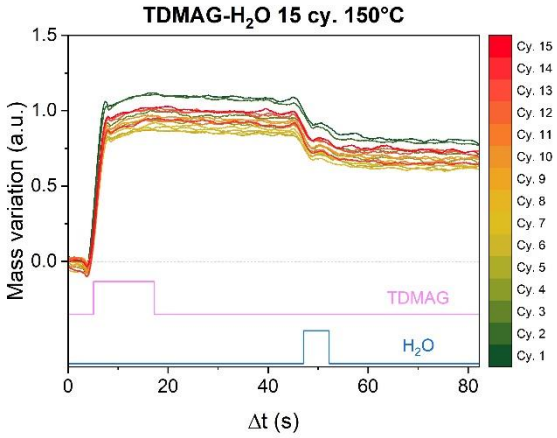



Figure S14: Overlay of consecutive cycles of ALD of $GaO_x$ measured by in situ QCM using **TDMAG** as gallium precursor. Green traces indicate initial cycles and red traces the last ones (15 total cycles).

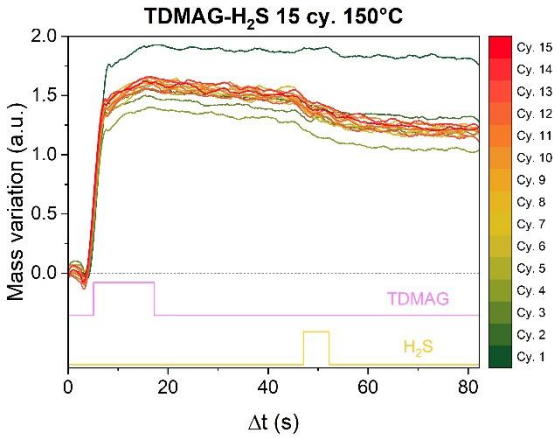



Figure S13: Overlay of consecutive cycles of ALD of $GaS_x$ measured by in situ QCM using **TDMAG** as gallium precursor. Green traces indicate initial cycles and red traces the last ones (15 total cycles).

**Modelling of the growth mechanism of $Ga_2S_3$ from TDMAG and $H_2S$**

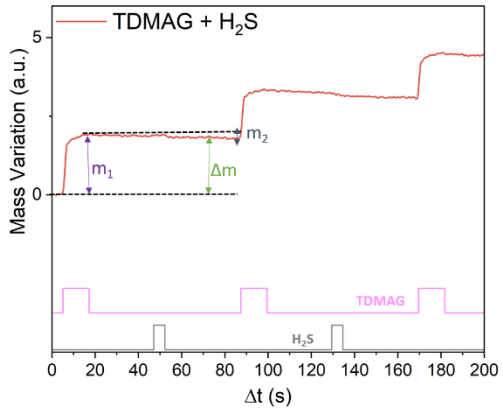



Figure S15: Mass variations measured by in situ QCM measurements during ALD of GaSx at $T_{dep}$ = 150°C using **TDMAG** and $H_2S$. The lower part of the graphs indicates the pulse sequence. (*Δm* corresponds to overall mass variation after one cycle and and $m_1$ to the mass variation after the pulse of metal precursor).

The $Ga_2S_3$ growth mechanism has already been attributed to the following surface reactions by Meng et al.[4]:

$$\vdash (SH)_n + Ga(NMe_2)_3 \rightarrow \vdash S_nGa(NMe_2)_{(3-n)} + n\,HNMe_2 \qquad \textit{Equation S1}$$

during the TDMAG pulse, and:

$$\vdash S_nGa(NMe_2)_{(3-n)} + 1.5\,H_2S \rightarrow \vdash S_{1.5}Ga(SH)_n + (3-n)HNMe_2 \qquad \textit{Equation S2}$$

during the $H_2S$ pulse, where "⊢" represent the surface species, *n* the number of ligand released during the TDMAG pulse. The n value can be determined from the (Δm / m1) ratio. In our case, (Δm / m1) = 0.82, which corresponds to *n* = 0.79, which is slightly higher than reported value ((Δm / m1) = 0.63, n = 0.32 at $T_{dep}$ = 200-250 °C).[4]

The same reasoning can be applied to the reaction with $H_2O$ in the place of $H_2S$.

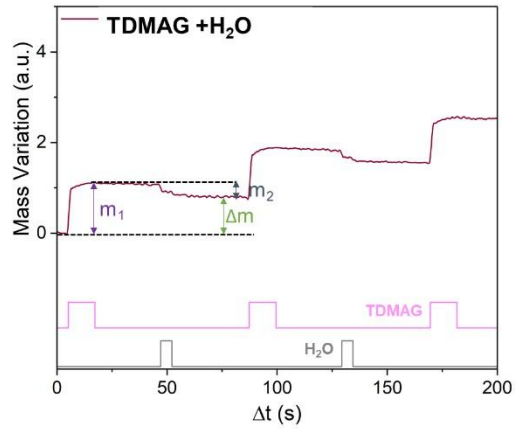



Figure S16: Mass variations measured by in situ QCM measurements during ALD of $GaO_x$ at $T_{dep}$ = 150°C using **TDMAG** and $H_2O$. The lower part of the graphs indicates the pulse sequence. (*Δm* corresponds to overall mass variation after one cycle and and $m_1$ to the mass variation after the pulse of metal precursor).

Parallel to the $H_2S$ case, the surface reactions can be described as follows:

$$\vdash (OH)_n + Ga(NMe_2)_3 \rightarrow \vdash O_nGa(NMe_2)_{(3-n)} + n\ HNMe_2 \qquad \textit{Equation S3}$$

during the TDMAG pulse, and:

$$\vdash O_nGa(NMe_2)_{(3-n)} + 1.5\ H_2O \rightarrow \vdash O_{1.5}Ga(OH)_n + (3-n)HNMe_2 \qquad \textit{Equation S4}$$

during the $H_2O$ pulse, where "⊢" represent the surface species, *n* the number of ligand released during the TDMAG pulse. The n value can be determined from the (Δm / m1) ratio. In our case, (Δm / m1) = 0.76, which corresponds to *n* = 2.05.

# 4. Thin film characterisation

## 4.1. Ellipsometry data

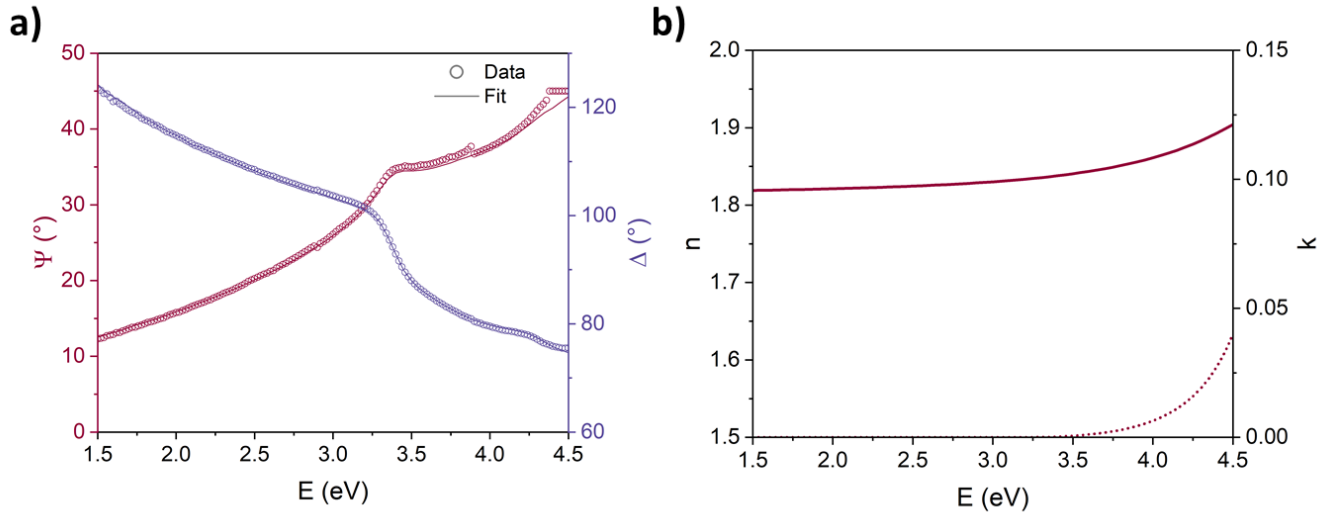



Figure S17: Spectroscopic ellipsometry data of the $Ga_2O_3$ film on Si 100 wafer produced by 400 ALD cycles of **$LGa(NMe_2)_2$** and $H_2O$ precursors. Dots: experimental values, solid line: data fitting. Fitting with $X^2$=0.112, yielding 22.9 nm thickness and 4.50 eV bandgap.

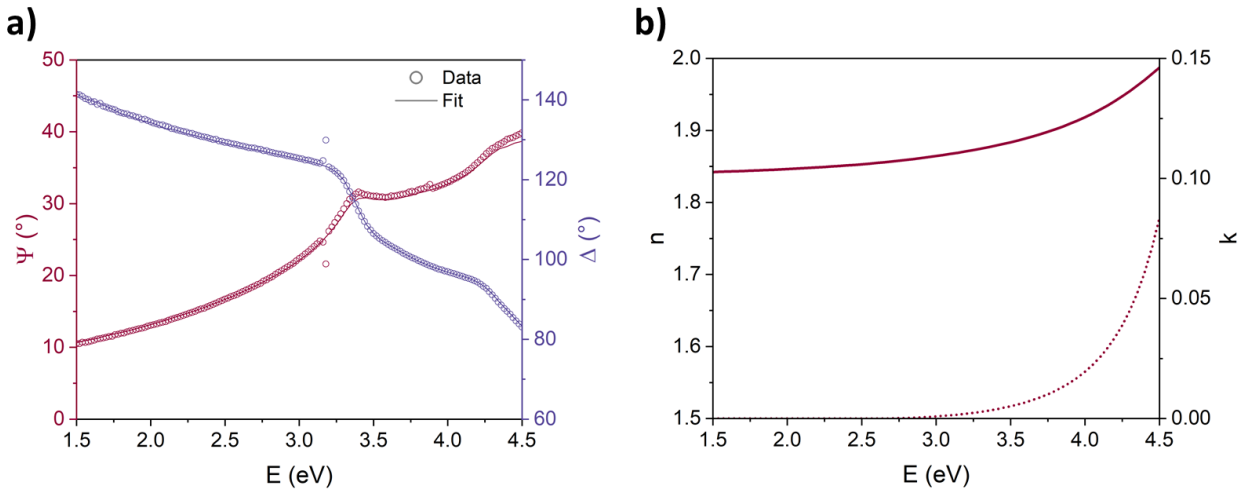



Figure S18: Spectroscopic ellipsometry data of the $Ga_2O_3$ film on Si 100 wafer produced by 150 ALD cycles of **TDMAG** and $H_2O$ precursors. Dots: experimental values, solid line: data fitting. Fitting with $X^2$=0.150, yielding 13.6 nm thickness and 4.45 eV bandgap.

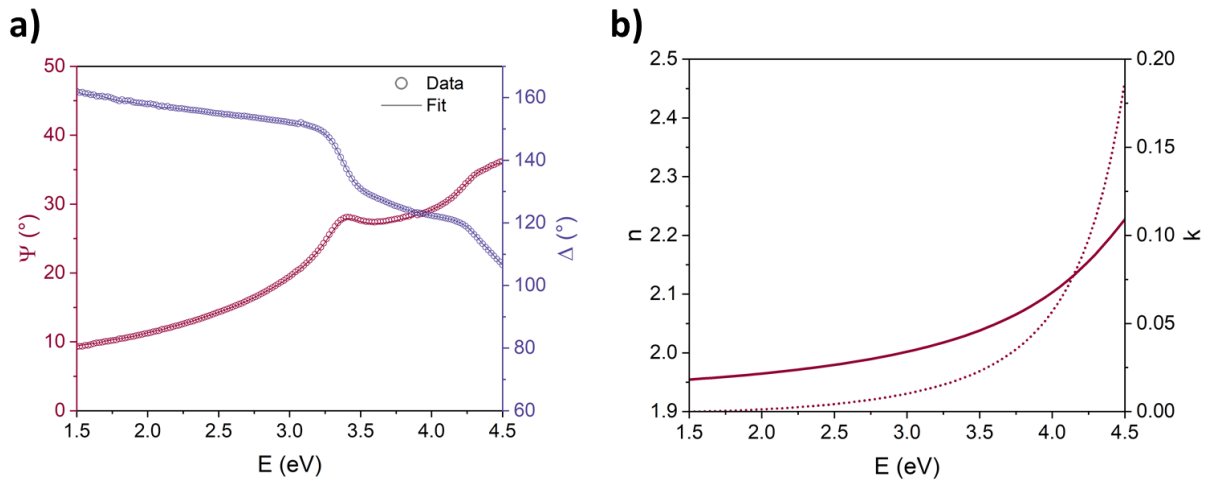



Figure S19: Spectroscopic ellipsometry data of the $Ga_2S_3$ film on Si 100 wafer produced by 400 ALD cycles of **$LGa(NMe_2)_2$** and $H_2S$ precursors. Dots: experimental values, solid line: data fitting. Fitting with $X^2$=0.052, yielding 5.1 nm thickness and 4.30 eV bandgap.

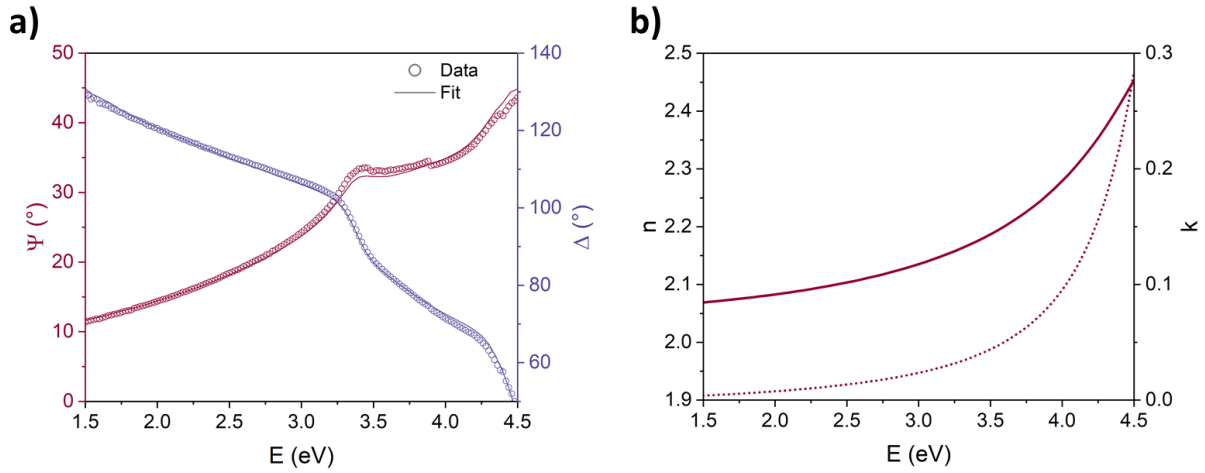



Figure S20: Spectroscopic ellipsometry data of the $Ga_2S_3$ film on Si 100 wafer produced by 150 ALD cycles of **TDMAG** and $H_2S$ precursors. Dots: experimental values, solid line: data fitting. Fitting with $X^2$=2.55, yielding 18.6 nm thickness and 3.95 eV bandgap.

## 4.2. X-ray Reflectometry (XRR) data

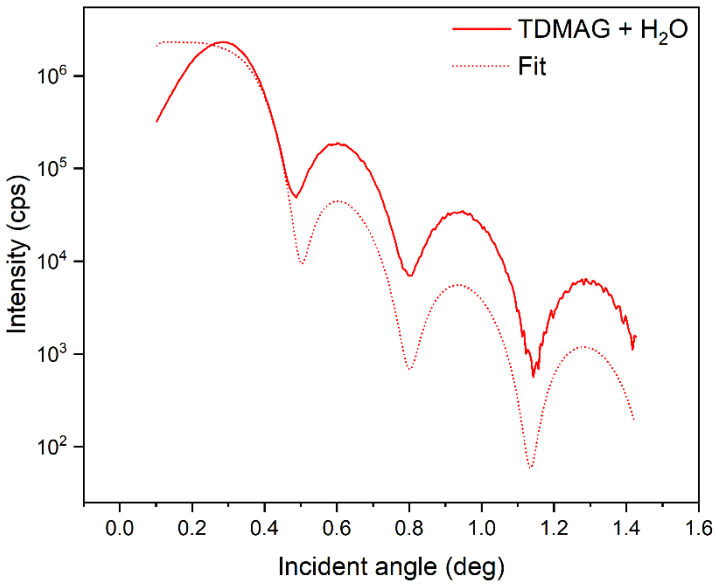



Figure S21: X-ray Reflectometry (XRR) data of the $Ga_2O_3$ film on Si 100 wafer produced by 150 ALD cycles of **TDMAG** and $H_2O$ precursors. Solid line: experimental values, dots: data fitting. Fitting finds a 12.3 nm film.

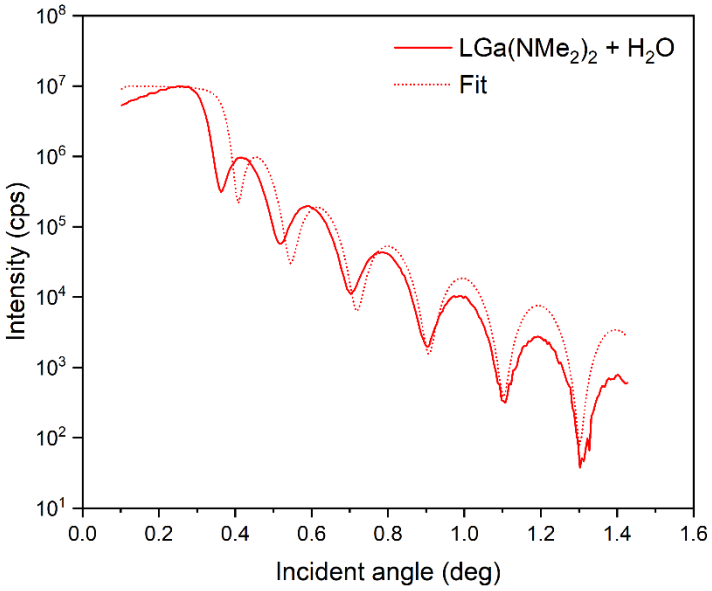



Figure S22: X-ray Reflectometry (XRR) data of the $Ga_2O_3$ film on Si 100 wafer produced by 400 ALD cycles of **$LGa(NMe_2)_2$** and $H_2O$ precursors. Solid line: experimental values, dots: data fitting. Fitting finds a 21.2 nm film.

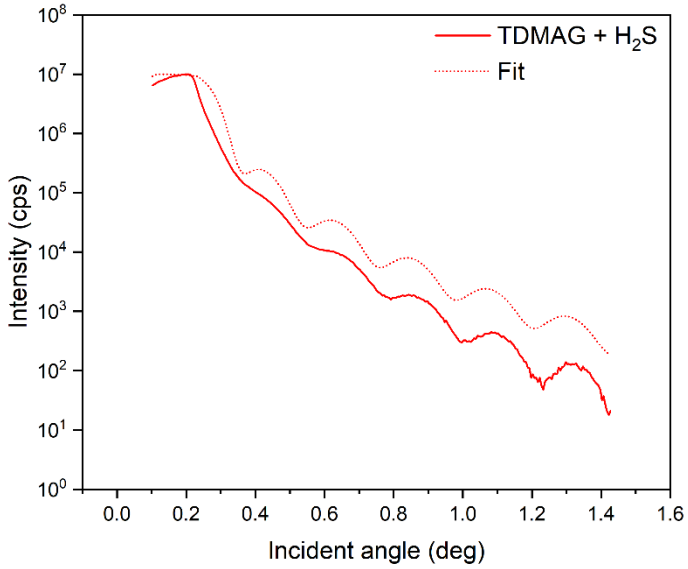



Figure S23: X-ray Reflectometry (XRR) data of the $Ga_2S_3$ film on Si 100 wafer produced by 150 ALD cycles of **TDMAG** and $H_2S$ precursors. Solid line: experimental values, dots: data fitting. Fitting finds a 22.9 nm film.

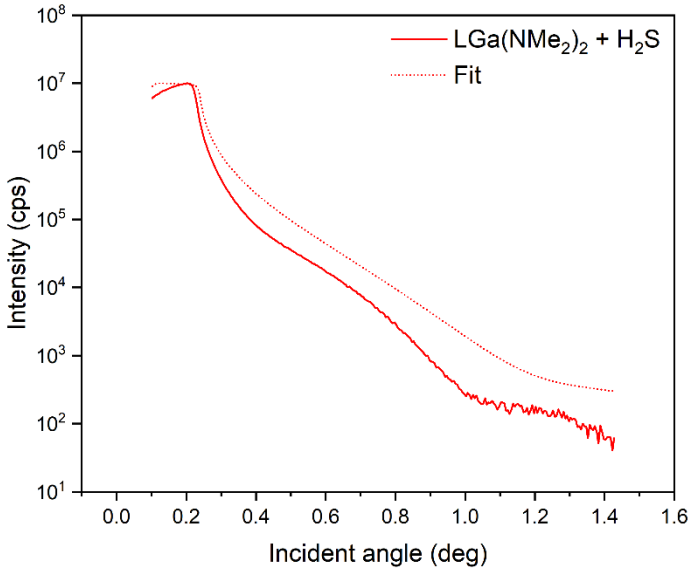



Figure S24: X-ray Reflectometry (XRR) data of the $Ga_2S_3$ film on Si 100 wafer produced by 400 ALD cycles of **$LGa(NMe_2)_2$** and $H_2S$ precursors. Solid line: experimental values, dots: data fitting. Fitting finds a 3.9 nm film.

## 4.3. X-ray Photoelectron Spectroscopy (XPS) data

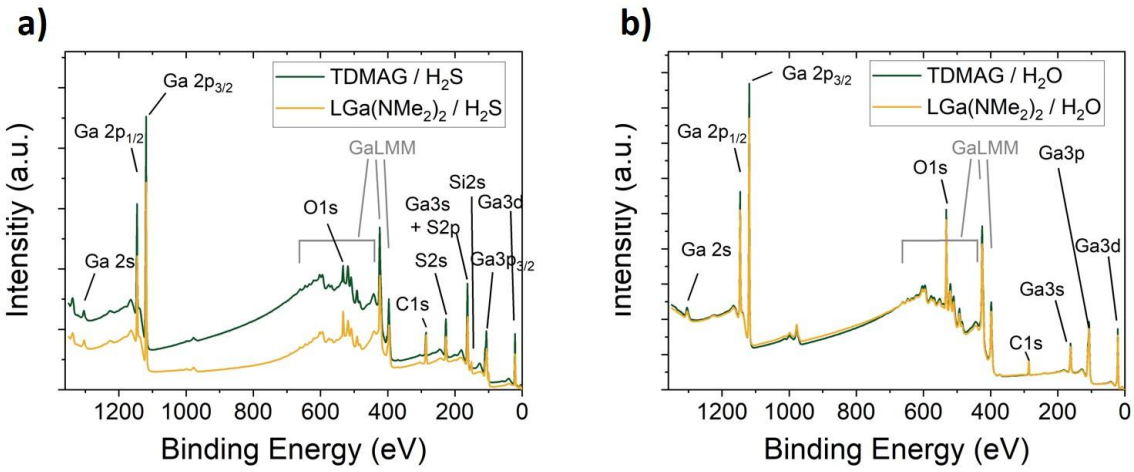



Figure S25: XPS survey spectra of thin films deposited on $Si_{ox}$/Si substrates: (a) $Ga_xS$ from **TDMAG**/$H_2S$ (dark green) and **LGa(NMe$_2$)$_2$** /$H_2S$ (orange); (a) $Ga_xO$ from **TDMAG**/$H_2O$ (green) and **LGa(NMe$_2$)$_2$** /$H_2O$ (orange)

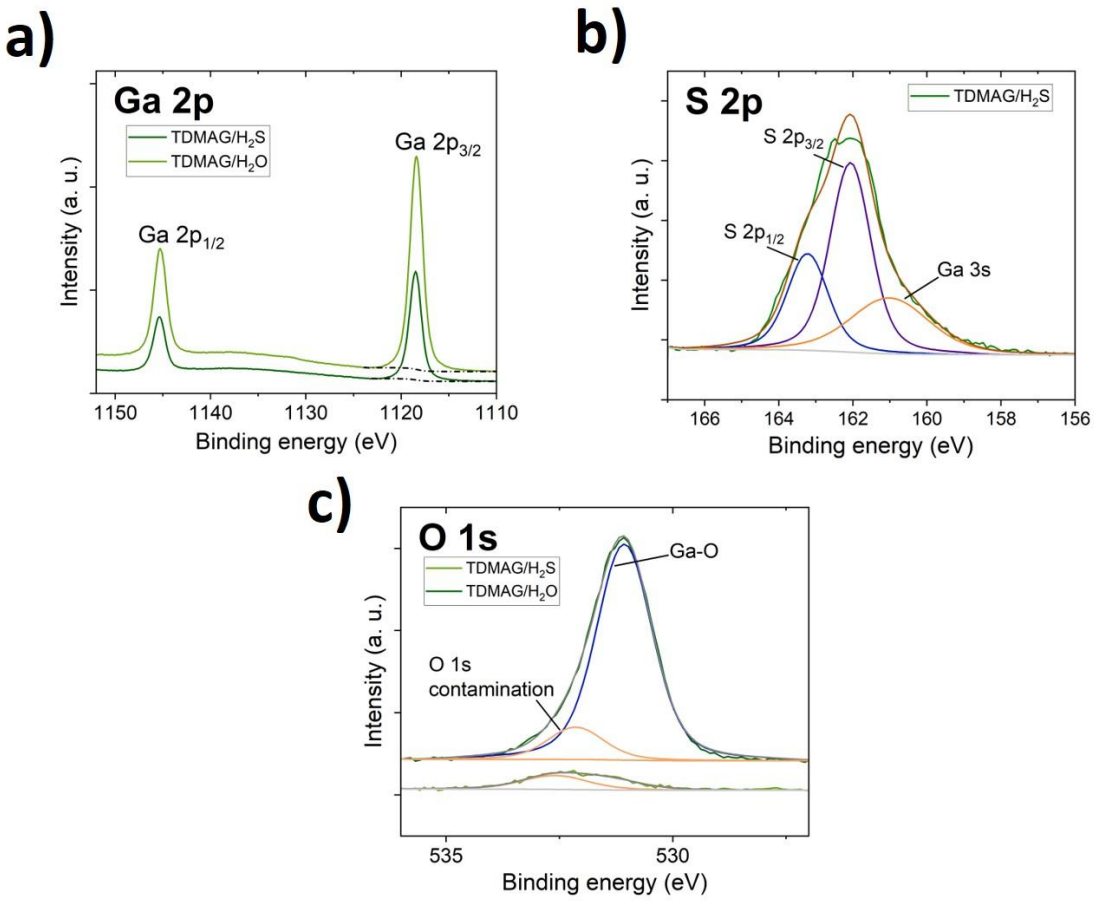



Figure S26: High energy resolution spectral regions of the main elements of Ga-containing films obtained from **TDMAG** precursor (a) Ga 2p (b) S 2p/Ga3s (c) O 1s.

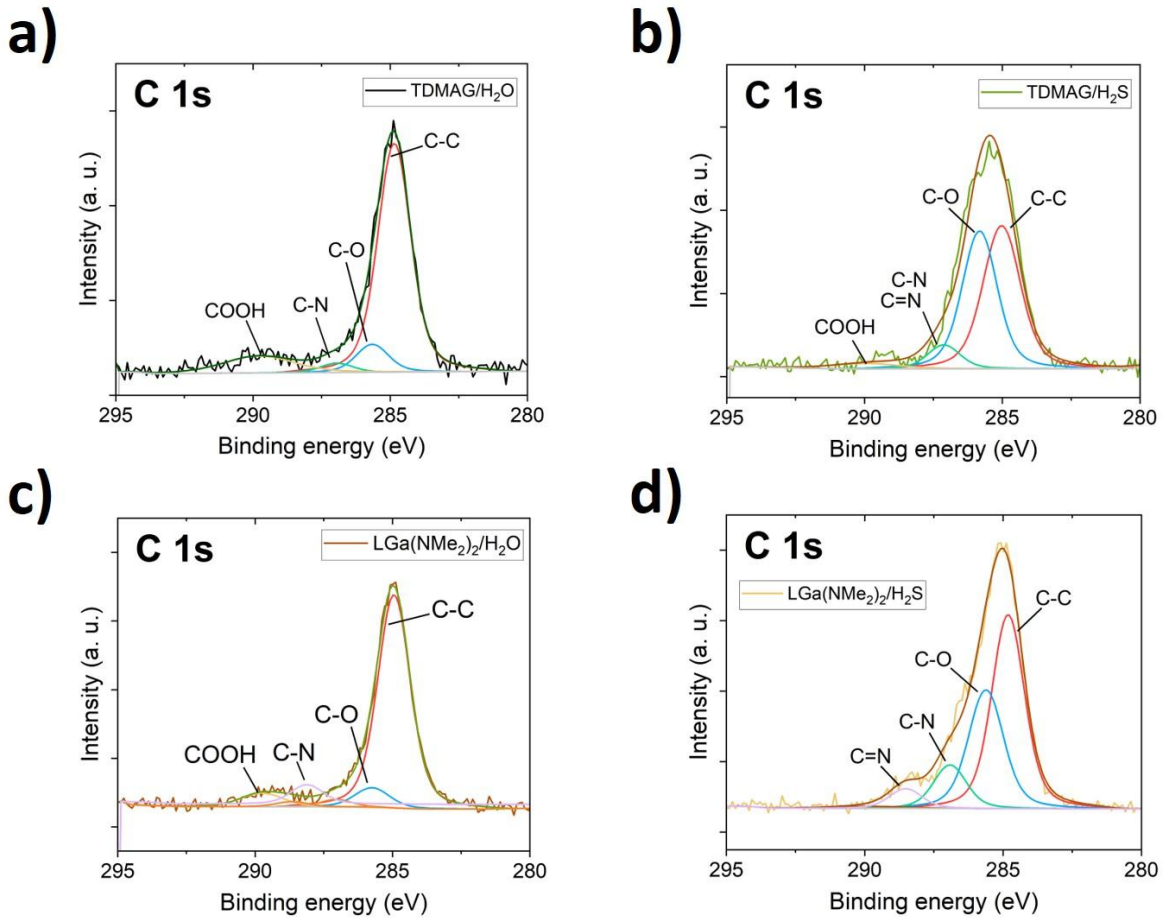



Figure S27: High energy resolution spectral regions of C 1s of Ga-containing films obtained from **TDMAG** precursor and (a) $H_2O$, (b) $H_2S$) and **LGa(NMe$_2$)$_2$** with (c) $H_2O$, and (d) $H_2S$) (Ar+-etching time = 0s).

Table S2: Atomic % compositions for the $GaY_x$ films obtained (Y=O, S).

| | Ga | S/O | O contamination | C contamination | N (C-N) |
|---|---|---|---|---|---|
| $GaS_x$/**TDMAG** | 30.10 | 34.59 | 9.03 | 24.47 | 1.81 |
| $GaS_x$/**LGa(NMe$_2$)$_2$** | 26.25 | 26.37 | 12.10 | 29.55 | 5.73 |
| $GaO_x$/**TDMAG** | 38.09 | 43.10 | 6.47 | 11.97 | 0.37 |
| $GaO_x$/**LGa(NMe$_2$)$_2$** | 34.62 | 46.14 | 4.10 | 14.42 | 0.71 |

## 5. DFT calculations

The reactions taken into consideration for DFT calculations are as follows.

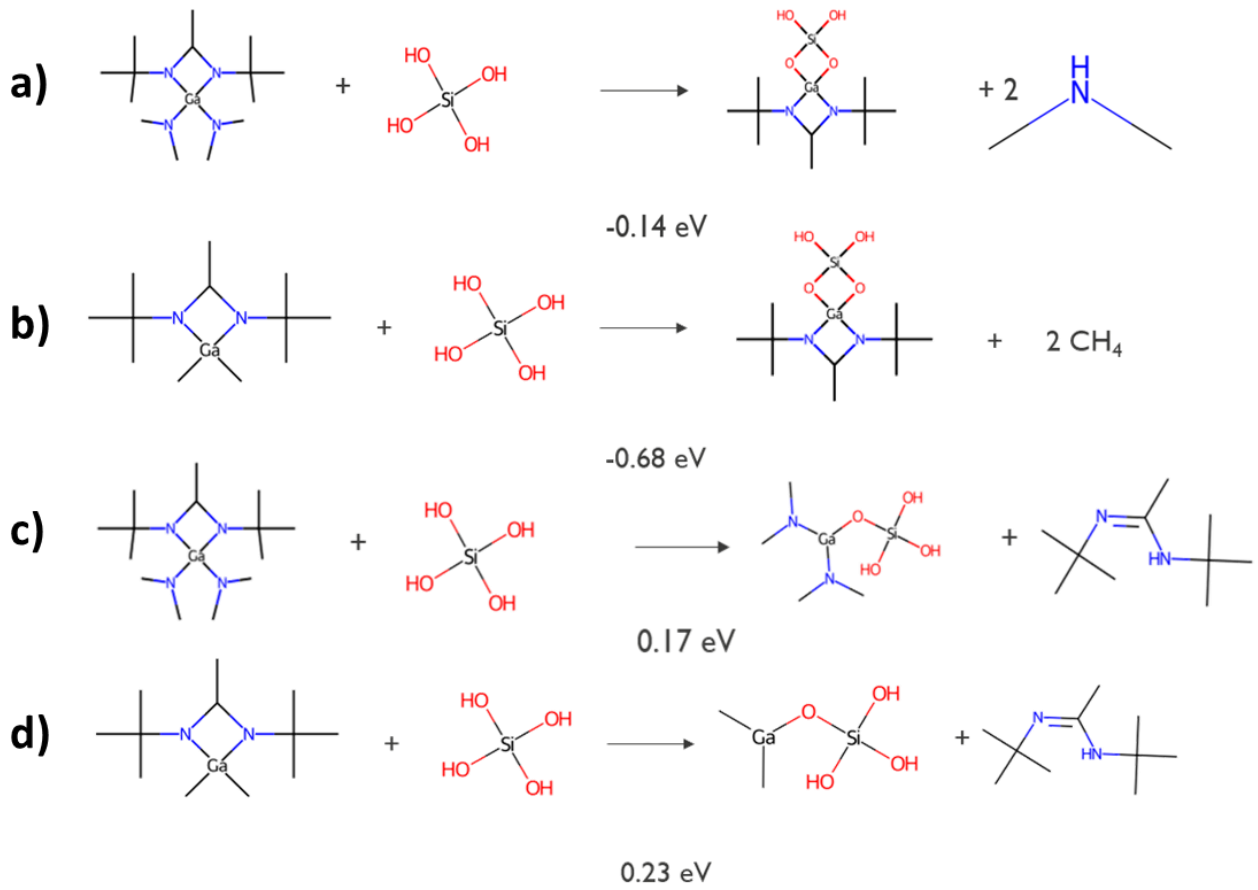



Figure S28: Surface reactions computed for DFT calculations following model A (a and b) and model B (c and d) for **$LGa(NMe_2)_2$** (a and c) and for **$LGaMe_2$** (b and d); the values represent the corresponding enthalpies. The structures formulas are made with RDKit.[5]

Table S3: Structural formulas and corresponding file names with the atomic positions that were relaxed with DFT are shown. The structures formulas are made with RDKit. [5] Optimized coordinates for each are given in Tables S3 to S11.

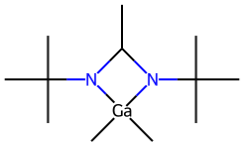
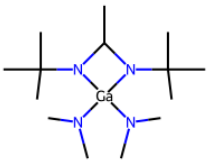
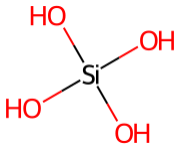
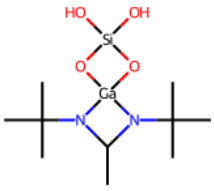
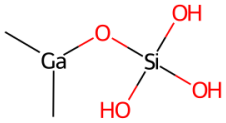
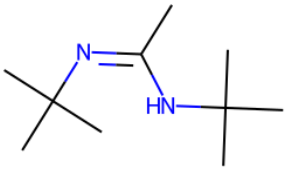
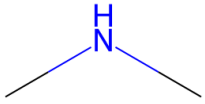
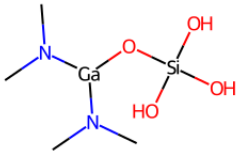
| Structural formula | File name with optimized atomic coordinates |
|---|---|
|  | prec1.xyz |
|  | prec2.xyz |
|  | SiOH4.xyz |
|  | product1.xyz |
| $CH_4$ | product2.xyz |
|  | product3.xyz |
|  | product4.xyz |
|  | product5.xyz |
|  | product6.xyz |

Table S3: Optimised molecular coordinates of “prec1”.

Lattice="18.05941000 0.00000000 0.00000000 0.00000000 16.50200000 0.00000000 0.00000000 0.00000000 16.65885000" pbc=[T, T, T] Properties=species:S:1:pos:R:3

| | | | |
|---|---|---|---|
| Ga | 9.57785987 | 9.55671075 | 8.11292655 |
| H | 9.20496880 | 5.74442313 | 11.07269288 |
| H | 9.49793572 | 7.36916930 | 11.73015403 |
| H | 10.73655631 | 6.10204482 | 11.88220144 |
| H | 10.48359834 | 5.01783103 | 8.87726832 |
| H | 12.00121435 | 5.30423096 | 9.74284905 |
| H | 11.68674631 | 6.12925409 | 8.19662617 |
| H | 11.33859694 | 8.84200658 | 10.76867866 |
| H | 12.21487585 | 8.33660665 | 9.30269293 |
| H | 12.50299670 | 7.49699801 | 10.84401354 |
| H | 8.48840270 | 5.25938188 | 9.02921358 |
| H | 7.10057399 | 5.76819247 | 8.04775338 |
| H | 7.15411662 | 6.15614292 | 9.77611259 |
| H | 6.71193946 | 6.41912085 | 6.17594225 |
| H | 7.52665445 | 7.68431747 | 5.23674914 |
| H | 5.74824664 | 7.60684220 | 5.28312289 |
| H | 5.38745573 | 7.13196059 | 8.35479210 |
| H | 4.50621950 | 8.36885307 | 7.44757819 |
| H | 5.46185910 | 8.82947916 | 8.87499795 |
| H | 7.41511226 | 10.10903713 | 5.91769934 |
| H | 6.55293766 | 10.59114618 | 7.39961994 |
| H | 5.64012535 | 10.01485529 | 5.98345476 |
| H | 11.76060150 | 9.95647971 | 6.77456876 |
| H | 10.35986643 | 10.41657826 | 5.79825361 |
| H | 10.78110561 | 8.69872528 | 5.98528095 |
| H | 8.60366903 | 10.74401532 | 10.19861415 |
| H | 8.77555687 | 11.90169623 | 8.85896643 |
| H | 10.19761496 | 11.42381586 | 9.79620198 |

| | | | |
|---|---|---|---|
| C | 10.60332640 | 6.98159336 | 9.88826921 |
| C | 9.96664546 | 6.51860349 | 11.21796265 |
| C | 11.22508809 | 5.78513883 | 9.13129250 |
| C | 11.73471258 | 7.97540167 | 10.22263029 |
| C | 8.45268821 | 7.37389155 | 8.57248380 |
| C | 7.76406322 | 6.06285963 | 8.86619785 |
| C | 6.65996242 | 8.42973034 | 7.09511537 |
| C | 6.66175649 | 7.47410051 | 5.87946320 |
| C | 5.43475314 | 8.16750588 | 7.99956265 |
| C | 6.55979845 | 9.87540784 | 6.56663788 |
| C | 10.73782247 | 9.66438292 | 6.50299632 |
| C | 9.25341238 | 11.05751131 | 9.37291226 |
| N | 9.66114288 | 7.72839998 | 9.03994786 |
| N | 7.93112901 | 8.36727905 | 7.83329658 |

Table S4: Optimised molecular coordinates of “prec2”.

Lattice="18.60063000 0.00000000 0.00000000 0.00000000 17.82771000 0.00000000 0.00000000 0.00000000 17.28835000" pbc=[T, T, T] Properties=species:S:1:pos:R:3

| | | | |
|---|---|---|---|
| Ga | 9.85238205 | 9.45473271 | 8.28647419 |
| H | 8.10555749 | 7.42624522 | 12.35956378 |
| H | 8.57251492 | 9.14026119 | 12.42218113 |
| H | 9.50310170 | 7.92292039 | 13.32389905 |
| H | 9.61331510 | 5.75223315 | 10.98706751 |
| H | 10.98069190 | 6.22247146 | 12.00859898 |
| H | 11.09918283 | 6.37068383 | 10.23825611 |
| H | 10.79536264 | 9.92010493 | 11.40999426 |
| H | 11.82922206 | 8.75935879 | 10.54817209 |
| H | 11.63871237 | 8.63487518 | 12.31347564 |
| H | 6.49779259 | 7.52561900 | 10.53479130 |
| H | 7.67487375 | 6.20406019 | 10.53254311 |
| H | 6.59743851 | 6.43056399 | 9.13943371 |

| | | | |
|---|---|---|---|
| H | 8.40734270 | 9.00658070 | 5.49318081 |
| H | 7.53999976 | 10.31960907 | 6.32199526 |
| H | 6.68875587 | 9.30790646 | 5.12851801 |
| H | 7.83504917 | 6.58870173 | 5.98747387 |
| H | 6.12533816 | 6.92878011 | 5.63038974 |
| H | 6.57399809 | 6.15902224 | 7.16010334 |
| H | 5.82417184 | 9.79108163 | 8.11408290 |
| H | 5.30443276 | 8.11673846 | 8.41027134 |
| H | 4.93651418 | 8.89152565 | 6.86257338 |
| H | 12.48105459 | 10.55236009 | 7.66002747 |
| H | 13.11922779 | 9.49500802 | 6.38028991 |
| H | 13.24208748 | 9.00296465 | 8.08276131 |
| H | 10.38665589 | 7.00848896 | 6.79854032 |
| H | 11.96237741 | 6.87186866 | 7.61643844 |
| H | 11.88692270 | 7.33336618 | 5.90294492 |
| H | 10.72142537 | 11.78940486 | 6.76177549 |
| H | 10.39600055 | 13.17417612 | 7.82889534 |
| H | 9.08152121 | 12.46560847 | 6.86668164 |
| H | 8.51167280 | 11.10539174 | 10.27378927 |
| H | 7.73108974 | 12.01536193 | 8.95708346 |
| H | 9.02282058 | 12.76924919 | 9.91519823 |
| C | 9.90543810 | 7.93566414 | 11.18051021 |
| C | 8.95902165 | 8.11295526 | 12.38837248 |
| C | 10.42435072 | 6.48275662 | 11.09745238 |
| C | 11.11607392 | 8.87026895 | 11.37724349 |
| C | 8.20063391 | 7.87846405 | 9.27742742 |
| C | 7.18661627 | 6.95168858 | 9.89861479 |
| C | 7.03406157 | 8.32050418 | 7.04860087 |
| C | 7.44133813 | 9.29852869 | 5.92767517 |
| C | 6.88258084 | 6.91392767 | 6.42658030 |
| C | 5.69685366 | 8.80320950 | 7.65095550 |

| | | | |
|---|---|---|---|
| C | 12.58456037 | 9.50496174 | 7.34662269 |
| C | 11.38442090 | 7.46148004 | 6.87798847 |
| C | 9.98662968 | 12.21889351 | 7.45540999 |
| C | 8.69895561 | 11.81752003 | 9.45833781 |
| N | 9.28228597 | 8.36189818 | 9.91405332 |
| N | 8.13845229 | 8.36294201 | 8.02625427 |
| N | 11.27655292 | 8.87250041 | 7.22184704 |
| N | 9.72183508 | 11.30239070 | 8.55847128 |

Table S5: Optimised molecular coordinates of “SiOH4”.

Lattice="13.53818000 0.00000000 0.00000000 0.00000000 13.49583000 0.00000000 0.00000000 0.00000000 13.05688000" pbc=[T, T, T] Properties=species:S:1:pos:R:3

| | | | |
|---|---|---|---|
| Si | 6.64875291 | 6.76109834 | 6.58077600 |
| H | 5.87956383 | 8.44043314 | 7.85148997 |
| H | 5.48331994 | 6.48385443 | 4.68451019 |
| H | 6.47035230 | 4.87330043 | 7.77591125 |
| H | 8.75789569 | 7.25624450 | 6.00369932 |
| O | 5.70799900 | 7.49489295 | 7.71849166 |
| O | 6.23069950 | 7.01216477 | 5.00620608 |
| O | 6.49825078 | 5.14097956 | 6.84377281 |
| O | 8.15984219 | 7.39553198 | 6.75475251 |

Table S6: Optimised molecular coordinates of “product1”.

Lattice="18.02654000 0.00000000 0.00000000 0.00000000 14.97671000 0.00000000 0.00000000 0.00000000 18.61824000" pbc=[T, T, T] Properties=species:S:1:pos:R:3

| | | | |
|---|---|---|---|
| Ga | 8.46629582 | 7.67669978 | 9.42098233 |
| Si | 5.98293506 | 7.69831726 | 9.54353003 |
| H | 11.07418011 | 9.32393246 | 12.06811492 |
| H | 12.53526691 | 8.39791193 | 11.65309287 |
| H | 11.82324150 | 8.24259923 | 13.26490501 |
| H | 8.85636451 | 8.13442072 | 12.50005574 |

| | | | |
|---|---|---|---|
| H | 9.66374416 | 7.04427891 | 13.65493491 |
| H | 8.74299844 | 6.36759386 | 12.29164992 |
| H | 12.32860798 | 5.78711787 | 11.31568331 |
| H | 10.73829595 | 5.02908183 | 11.54040762 |
| H | 11.63791282 | 5.66257305 | 12.93975504 |
| H | 12.85470275 | 7.07324946 | 9.85644372 |
| H | 12.74867754 | 8.69041914 | 9.12765759 |
| H | 12.67943487 | 7.25242142 | 8.09528636 |
| H | 9.95633714 | 5.96118968 | 6.34923522 |
| H | 11.66366564 | 6.44087072 | 6.46748953 |
| H | 10.72909313 | 6.86294356 | 5.02366774 |
| H | 8.09841414 | 7.67905070 | 6.40370547 |
| H | 8.89203550 | 8.59484246 | 5.10151848 |
| H | 8.47710829 | 9.40309086 | 6.63307553 |
| H | 12.23511237 | 8.99802869 | 6.74259515 |
| H | 10.89731752 | 10.15569333 | 6.93623939 |
| H | 11.22318801 | 9.41484789 | 5.35363917 |
| H | 4.10965511 | 7.77204353 | 8.34358397 |
| H | 5.31288751 | 6.75219561 | 11.45739292 |
| C | 10.68079643 | 7.20296906 | 11.73046064 |
| C | 11.58539113 | 8.36119796 | 12.19897043 |
| C | 9.40679927 | 7.18839517 | 12.59755885 |
| C | 11.39190419 | 5.84136236 | 11.88396754 |
| C | 10.88038637 | 7.65380844 | 9.20541602 |
| C | 12.37631564 | 7.65771011 | 9.06639380 |
| C | 10.22024664 | 8.08848348 | 6.75510225 |
| C | 10.67395721 | 6.75894681 | 6.11611577 |
| C | 8.83727599 | 8.46468535 | 6.19000686 |
| C | 11.20856290 | 9.22917770 | 6.43630357 |
| N | 10.20670069 | 7.40382344 | 10.34465299 |
| N | 10.01684846 | 7.92999962 | 8.21111456 |

| | | | |
|---|---|---|---|
| O | 7.10049793 | 8.88831336 | 9.86252111 |
| O | 4.99238537 | 8.16968428 | 8.30749308 |
| O | 4.92292010 | 7.30023393 | 10.75962214 |
| O | 7.04886696 | 6.46064599 | 9.19630531 |

Table S7: Optimised molecular coordinates of “product2”.

Lattice="11.47920000 0.00000000 0.00000000 0.00000000 11.66469000 0.00000000 0.00000000 0.00000000 11.79903000" pbc=[T, T, T] Properties=species:S:1:pos:R:3

| | | | |
|---|---|---|---|
| H | 6.83672566 | 5.83240556 | 5.89947326 |
| H | 5.37379376 | 6.24054223 | 6.85007663 |
| H | 5.37377189 | 4.80517872 | 5.77759870 |
| H | 5.37380546 | 6.45167336 | 5.07067258 |
| C | 5.73949814 | 5.83248094 | 5.89942927 |

Table S8: Optimised molecular coordinates of “product3”.

Lattice="16.13380000 0.00000000 0.00000000 0.00000000 16.56252000 0.00000000 0.00000000 0.00000000 13.21898000" pbc=[T, T, T] Properties=species:S:1:pos:R:3

| | | | |
|---|---|---|---|
| Ga | 9.45482233 | 9.22209448 | 6.60754690 |
| Si | 6.97062742 | 7.33580084 | 6.99091318 |
| H | 6.35645106 | 7.00451408 | 9.11634423 |
| H | 5.23590521 | 8.16458823 | 5.83703163 |
| H | 7.38632498 | 5.28863578 | 6.18872879 |
| H | 8.07227640 | 9.67601662 | 4.52752455 |
| H | 9.24756058 | 8.38840883 | 4.21208099 |
| H | 9.78602520 | 10.09512547 | 4.19927627 |
| H | 11.78233622 | 9.69047077 | 7.56128341 |
| H | 10.56631442 | 9.64807923 | 8.87049919 |
| H | 10.72570601 | 11.08789287 | 7.82063832 |
| C | 9.11652689 | 9.37357806 | 4.67985973 |
| C | 10.76622145 | 9.99119281 | 7.84947873 |
| O | 6.23584714 | 6.56386055 | 8.26092836 |

| | | | |
|---|---|---|---|
| O | 6.02888998 | 8.50228374 | 6.28135634 |
| O | 7.17075756 | 6.16502252 | 5.83430828 |
| O | 8.31940898 | 8.06924711 | 7.50878504 |

Table S9: Optimised molecular coordinates of “product4”.

Lattice="18.37766000 0.00000000 0.00000000 0.00000000 14.28497000 0.00000000 0.00000000 0.00000000 15.28557000" pbc=[T, T, T] Properties=species:S:1:pos:R:3

| | | | |
|---|---|---|---|
| H | 8.36513921 | 7.81303035 | 5.69931921 |
| H | 7.31724789 | 9.03944650 | 6.43036723 |
| H | 6.65332091 | 7.87127072 | 5.26487781 |
| H | 8.04071507 | 5.26105355 | 6.49780659 |
| H | 6.33425804 | 5.36589749 | 6.03949630 |
| H | 6.78859942 | 4.92957746 | 7.70289485 |
| H | 5.40472568 | 8.40617307 | 7.96368232 |
| H | 5.18574481 | 6.72422008 | 8.47464313 |
| H | 4.82762748 | 7.19198364 | 6.78945615 |
| H | 8.74225551 | 7.91041935 | 10.60724983 |
| H | 10.34703386 | 8.34080615 | 9.95858190 |
| H | 10.02203192 | 6.67278910 | 10.46033655 |
| H | 9.45254529 | 6.60442183 | 6.76166511 |
| H | 11.36975862 | 9.08472924 | 8.24225498 |
| H | 11.08497879 | 8.95685790 | 6.49577095 |
| H | 12.71928437 | 8.70759736 | 7.15382653 |
| H | 12.08440892 | 6.94097361 | 9.56014381 |
| H | 13.27151704 | 6.45953081 | 8.34158513 |
| H | 11.93943828 | 5.35765110 | 8.76408066 |
| H | 11.16285255 | 6.71546585 | 5.31543114 |
| H | 11.55253208 | 5.23578204 | 6.23094866 |
| H | 12.80384797 | 6.46675460 | 5.93747914 |
| C | 6.97019147 | 7.05718259 | 7.26893302 |
| C | 7.35837345 | 7.99349400 | 6.09869117 |

| | | | |
|---|---|---|---|
| C | 7.04799631 | 5.57012946 | 6.84944163 |
| C | 5.50181561 | 7.36217857 | 7.63947634 |
| C | 9.02058979 | 7.23027978 | 8.62246155 |
| C | 9.57584344 | 7.56013288 | 9.99103433 |
| C | 11.36212048 | 7.02307053 | 7.47773898 |
| C | 11.64972818 | 8.53267551 | 7.33646026 |
| C | 12.20763928 | 6.41061846 | 8.61036868 |
| C | 11.74001654 | 6.31550604 | 6.16172380 |
| N | 7.73589181 | 7.33661998 | 8.49808694 |
| N | 9.90796922 | 6.75524890 | 7.65498136 |

Table S10: Optimised molecular coordinates of “product5”.

Lattice="13.47423000 0.00000000 0.00000000 0.00000000 12.28135000 0.00000000 0.00000000 0.00000000 13.04699000" pbc=[T, T, T] Properties=species:S:1:pos:R:3

| | | | |
|---|---|---|---|
| H | 6.03885685 | 5.97493940 | 7.74264462 |
| H | 6.19410252 | 6.22065943 | 4.81350517 |
| H | 4.79852779 | 5.67526290 | 5.75924557 |
| H | 6.25034370 | 4.64176997 | 5.62870544 |
| H | 8.28860938 | 6.94135665 | 6.10884628 |
| H | 8.32213702 | 5.35489335 | 6.91030200 |
| H | 8.22328601 | 6.85427446 | 7.87734253 |
| C | 5.89570188 | 5.68414628 | 5.72549963 |
| C | 7.88220348 | 6.36793412 | 6.95422355 |
| N | 6.41952658 | 6.39353197 | 6.89424796 |

Table S11: Optimised molecular coordinates of “product6”.

Lattice="17.47975000 0.00000000 0.00000000 0.00000000 17.91416000 0.00000000 0.00000000 0.00000000 13.57455000" pbc=[T, T, T] Properties=species:S:1:pos:R:3

| | | | |
|---|---|---|---|
| Ga | 9.32253571 | 8.25050479 | 6.46516461 |
| Si | 7.54801473 | 10.66323460 | 7.35430671 |
| H | 6.29204577 | 11.40378261 | 5.65260534 |

| | | | |
|---|---|---|---|
| H | 6.33194039 | 9.82205023 | 9.04491912 |
| H | 8.49171437 | 12.52404431 | 8.16016830 |
| H | 9.72160968 | 5.33466517 | 6.52331328 |
| H | 8.54253332 | 4.78768791 | 5.31420128 |
| H | 8.04121316 | 5.02335660 | 7.00587551 |
| H | 6.73834903 | 8.04169329 | 5.27880781 |
| H | 6.25256640 | 6.66400919 | 6.29195917 |
| H | 6.72702753 | 6.39990998 | 4.59282983 |
| H | 10.91279048 | 10.41808236 | 7.39922585 |
| H | 12.54145846 | 9.93231195 | 6.86764750 |
| H | 11.95724084 | 9.47397190 | 8.48706000 |
| H | 11.60639861 | 6.38670291 | 6.38418407 |
| H | 12.29948725 | 6.96231170 | 7.92146126 |
| H | 12.96249432 | 7.52418208 | 6.36859526 |
| C | 8.67775768 | 5.43006348 | 6.20077276 |
| C | 6.94769162 | 6.98814661 | 5.49911677 |
| C | 11.65284965 | 9.60925349 | 7.43538597 |
| C | 12.02854305 | 7.26140551 | 6.89400873 |
| N | 8.34645357 | 6.81564146 | 5.88464376 |
| N | 11.09907499 | 8.38355183 | 6.86634110 |
| O | 6.53808652 | 11.69711776 | 6.54315929 |
| O | 6.77012168 | 9.49933129 | 8.24237600 |
| O | 8.32770608 | 11.61688147 | 8.46076508 |
| O | 8.48849984 | 9.88058691 | 6.29499901 |

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