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Kinetic modeling has been used to study the decomposition chemistry of ammonia at a wide range of temperatures, pressures, concentrations, and carrier gases mimicking the conditions in chemical vapor deposition (CVD) of metal nitrides. The modeling show that only a small fraction of the ammonia molecules will decompose at most conditions studied. This suggests that the fact that high NH_3 to metal ratios often are employed in CVD is due to the very low amount of reactive decomposition products being formed rather than due to rapid decomposition of ammonia into stable dinitrogen and dihydrogen as suggested by purely thermodynamic equilibrium models.

I. INTRODUCTION

The metal nitride compounds constitute a technologically very important class of materials. Transition metal nitrides can be either insulating or conducting, depending on the oxidation state of the metal¹, while p-block metals form semiconducting nitrides with bandgaps ranging from infrared to ultraviolet²⁻⁴. Important examples are tantalum nitride, which forms diffusion barriers in copper interconnects in device structures⁵, silicon

nitride which forms insulating dielectric layers⁶ and gallium nitride which forms the basis for all blue light emitting diodes.⁷ Several transition metal nitrides are also very hard materials with applications in the coatings industry e.g. titanium nitride which can be applied as a golden colored hard coating on cutting tools.⁸

All examples above require that a thin film of the nitride is formed on a surface. One of the most important techniques for depositing nitride thin films is chemical vapor deposition (CVD).⁹ Given the inertness of dinitrogen, N_2 , in thermal CVD, the most common CVD precursor for nitrogen is ammonia, NH_3 . It should be noted that some CVD processes do use N_2 as nitrogen precursor, but then rather in the form of a N_2 - H_2 gas mixture as carrier gas, utilizing an extremely small fraction of all N_2 molecules in the gas mixture.¹⁰ But the reactivity of NH_3 is not properly matched to most metal CVD precursors as seen from the often very high NH_3 to metal precursor ratios used; CVD of semiconductor grade AlN and GaN uses NH_3 to trimethyl metal ratios of several hundred.¹¹

From a purely thermodynamic equilibrium point of view NH_3 should under CVD conditions decompose to N_2 and H_2 , i.e. the reverse of the Haber-Bosch process. The occurrence of a quick decomposition to inert N_2 has been used to explain the very high NH_3 to metal ratios used in nitride CVD.¹² However, this line of reasoning is not supported by observations of the NH_3 to metal ratios needed in the CVD of the group 13 nitrides, AlN, GaN and InN. InN forms a temperature sensitive crystal lattice which decomposes to metallic In and N_2 at 550 °C, forcing CVD of InN to be performed at lower temperatures than AlN and GaN which is carried out at 800-1000 °C. The lower CVD temperature should give a lower degree of decomposition of NH_3 to N_2 and H_2 if an

equilibrium is assumed to be prevalent and therefore require a lower $\text{NH}_3/\text{InMe}_3$ ratio, but the opposite is observed; CVD of InN requires $\text{NH}_3/\text{InMe}_3$ ratios of 10 000 – 100 000.¹³

Previous studies on NH_3 decomposition kinetics show that the decomposition is limited, especially at lower temperatures.^{14–16} Monnery et al.¹⁷ found that at close to atmospheric pressure and at temperatures between 1123 and 1423 K less than 25 % NH_3 had decomposed at residence times of 50-800 ms.

The present study presents an in-depth investigation of the time-resolved NH_3 reaction kinetics over a wide range of conditions obtainable during CVD. The decomposition of NH_3 at CVD conditions is studied by kinetic modelling using reaction mechanisms and reaction rate data from the literature.¹⁸ We find that the decomposition of NH_3 is very slow and the decomposition products will not reach their highest partial pressures during the typical residence time in the CVD reactor. We argue that this slow decomposition kinetics of NH_3 explains the very high NH_3 to metal precursor ratios needed in CVD processes.

II. MODELLING

From a known set of reaction mechanisms and the reaction steps involved, the reaction rate of each participating specimen (molecule, free atom, ion or radical) can, by kinetic reaction rate theory, be expressed as a function of the concentrations and the rate constants of each reaction step.¹⁹ The reaction rate functions for all the species constitute a differential equation system, the solution of which gives the time evolution of the amounts of the species. The kinetic model, i.e. the set of reaction mechanisms, used was developed by Konnov and de Ruyck for ammonia decomposition in shock waves.¹⁸ The rate constants in the model were optimized by them to give accurate results for the

decomposition concentrations and time evolution, especially the peak mole fractions and time to peak mole fraction for NH and NH₂ radicals. The model is accurate within experimental variation at lower temperatures but starts to deviate at temperatures higher than 2800 K (10-30 % for the mole fraction of NH and NH₃).¹⁸ Since 2800 K is much higher than the temperatures expected during CVD the model is expected to be accurate under the investigated conditions.

The model contained 51 reversible reactions and 11 species, 10 of which could directly participate in the decomposition of ammonia together with argon that could act as an inert third-body reactant, see Table I. The forward reaction rate was calculated from an Arrhenius-type equation using the parameters specified in the model. The reverse reaction rate was calculated from thermodynamic balance using thermodynamic data obtained from the Chemkin thermodynamic database.^{20,21} All kinetic modelling was performed using the Reaction engineering module from the COMSOL Multiphysics® simulation software.²²

TABLE I. Reaction steps and corresponding rate constant data used in the model. Constants are given for a modified Arrhenius expression $k = A \times \left(\frac{T}{T_0}\right)^n \times e^{-E_a/RT}$.

	Formula	A (M ^{1-order} s ⁻¹)	n	E _a (kJ mol ⁻¹)	Ref.
1 ^{a)}	H + H + M → H ₂ + M	6.50e+11	-1.0	0.000	23
2	H + H + H ₂ → H ₂ + H ₂	1.00e+11	-0.6	0.000	23
3 ^{b)}	N ₂ + M → N + N + M	3.70e+18	0.0	941.400	24
4	NH + M → N + H + M	2.65e+11	0.0	315.892	25
5	NH + H → N + H ₂	3.20e+10	0.0	1.360	26
6	NH + N → N ₂ + H	6.30e+08	0.5	0.000	27

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7	$\text{NH} + \text{NH} \rightarrow \text{N}_2 + \text{H} + \text{H}$	2.54e+10	0.0	0.000	28
8	$\text{NH} + \text{NH} \rightarrow \text{NNH} + \text{H}$	8.00e+08	0.5	4.184	24
9	$\text{NH} + \text{NH} \rightarrow \text{NH}_2 + \text{N}$	2.00e+08	0.5	8.368	24
10	$\text{NH} + \text{NH} \rightarrow \text{N}_2 + \text{H}_2$	1.00e+05	1.0	0.000	29
11	$\text{NH}_2 + \text{M} \rightarrow \text{NH} + \text{H} + \text{M}$	3.16e+20	-2.0	382.418	24
12	$\text{NH} + \text{H}_2 \rightarrow \text{NH}_2 + \text{H}$	1.00e+11	0.0	83.973	30
13	$\text{NH}_2 + \text{N} \rightarrow \text{N}_2 + \text{H} + \text{H}$	6.90e+10	0.0	0.000	31
14	$\text{NH}_2 + \text{NH} \rightarrow \text{N}_2\text{H}_2 + \text{H}$	1.50e+12	0.5	0.000	32
15	$\text{NH}_2 + \text{NH} \rightarrow \text{NH}_3 + \text{N}$	1.00e+10	0.0	0.837	33
16	$\text{NH}_2 + \text{NH}_2 \rightarrow \text{NH}_3 + \text{NH}$	5.00e+10	0.0	41.840	32
17	$\text{NH}_2 + \text{NH}_2 \rightarrow \text{N}_2\text{H}_2 + \text{H}_2$	3.00e+10	0.0	5.021	24
18	$\text{NH}_2 + \text{NH}_2 \rightarrow \text{N}_2\text{H}_3 + \text{H}$	7.40e+08	0.0	10.460	34
19	$\text{NH}_3 + \text{M} \rightarrow \text{NH}_2 + \text{H} + \text{M}$	2.20e+13	0.0	391.078	32
20	$\text{NH}_3 + \text{M} \rightarrow \text{NH} + \text{H}_2 + \text{M}$	6.30e+11	0.0	390.744	24
21	$\text{NH}_3 + \text{H} \rightarrow \text{NH}_2 + \text{H}_2$	5.42e+02	2.4	41.505	35
22	$\text{NH}_3 + \text{NH}_2 \rightarrow \text{N}_2\text{H}_3 + \text{H}_2$	1.00e+08	0.5	90.374	18
23	$\text{NNH} \rightarrow \text{N}_2 + \text{H}$	3.00e+08	0.0	0.000	36
24	$\text{NNH} + \text{M} \rightarrow \text{N}_2 + \text{H} + \text{M}$	1.00e+10	0.5	12.803	36
25	$\text{NNH} + \text{H} \rightarrow \text{N}_2 + \text{H}_2$	4.00e+10	0.5	12.552	24
26	$\text{NNH} + \text{N} \rightarrow \text{NH} + \text{N}_2$	3.00e+10	0.0	8.368	24
27	$\text{NNH} + \text{NH} \rightarrow \text{N}_2 + \text{NH}_2$	2.00e+08	0.5	8.368	24
28	$\text{NNH} + \text{NH}_2 \rightarrow \text{N}_2 + \text{NH}_3$	1.00e+10	0.0	0.000	34
29	$\text{NNH} + \text{NNH} \rightarrow \text{N}_2\text{H}_2 + \text{N}_2$	1.00e+10	0.0	41.840	24
30 ^{c)}	$\text{N}_2\text{H}_2 + \text{M} \rightarrow \text{NNH} + \text{H} + \text{M}$	5.00e+13	0.0	209.200	37
31	$\text{N}_2\text{H}_2 + \text{M} \rightarrow \text{NH} + \text{NH} + \text{M}$	3.16e+13	0.0	415.890	24
32	$\text{N}_2\text{H}_2 + \text{H} \rightarrow \text{NNH} + \text{H}_2$	5.00e+10	0.0	4.184	37

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33	$\text{N}_2\text{H}_2 + \text{NH} \rightarrow \text{NNH} + \text{NH}_2$	1.00e+10	0.0	4.184	24
34	$\text{N}_2\text{H}_2 + \text{NH}_2 \rightarrow \text{NH}_3 + \text{NNH}$	1.00e+10	0.0	16.736	24
35	$\text{N}_2\text{H}_2 + \text{NH}_2 \rightarrow \text{NH} + \text{N}_2\text{H}_3$	1.00e+08	0.5	141.336	24
36	$\text{N}_2\text{H}_2 + \text{N}_2\text{H}_2 \rightarrow \text{NNH} + \text{N}_2\text{H}_3$	1.00e+10	0.0	41.840	24
37	$\text{N}_2\text{H}_3 + \text{M} \rightarrow \text{NH}_2 + \text{NH} + \text{M}$	1.00e+13	0.0	174.598	24
38	$\text{N}_2\text{H}_3 + \text{M} \rightarrow \text{N}_2\text{H}_2 + \text{H} + \text{M}$	1.00e+13	0.0	207.945	24
39	$\text{N}_2\text{H}_3 + \text{H} \rightarrow \text{N}_2\text{H}_2 + \text{H}_2$	1.00e+09	0.0	0.837	24
40	$\text{N}_2\text{H}_3 + \text{H} \rightarrow \text{NH} + \text{NH}_3$	1.00e+08	0.0	0.000	24
41	$\text{N}_2\text{H}_3 + \text{NH}_2 \rightarrow \text{N}_2\text{H}_2 + \text{NH}_3$	1.00e+08	0.5	0.000	24
42	$\text{N}_2\text{H}_3 + \text{N}_2\text{H}_2 \rightarrow \text{N}_2\text{H}_4 + \text{NNH}$	1.00e+10	0.0	41.840	24
43	$\text{N}_2\text{H}_3 + \text{N}_2\text{H}_3 \rightarrow \text{NH}_3 + \text{NH}_3 + \text{N}_2$	1.00e+09	0.0	0.000	38
44 ^{d)}	$\text{N}_2\text{H}_4(+\text{M}) \rightarrow \text{NH}_2 + \text{NH}_2(+\text{M})$	7.90e+13	0.0	230.120	39
44 ^{e)}	$\text{N}_2\text{H}_4(+\text{M}) \rightarrow \text{NH}_2 + \text{NH}_2(+\text{M})$	4.46e+12	0.0	171.544	39
45	$\text{N}_2\text{H}_4 + \text{M} \rightarrow \text{N}_2\text{H}_3 + \text{H} + \text{M}$	1.00e+12	0.0	266.102	24
46	$\text{N}_2\text{H}_4 + \text{H} \rightarrow \text{N}_2\text{H}_3 + \text{H}_2$	5.94e+09	0.0	9.958	40
47	$\text{N}_2\text{H}_4 + \text{H} \rightarrow \text{NH}_2 + \text{NH}_3$	4.46e+06	0.0	12.970	41
48	$\text{N}_2\text{H}_4 + \text{N} \rightarrow \text{N}_2\text{H}_3 + \text{NH}$	7.50e+07	0.0	0.000	42
49	$\text{N}_2\text{H}_4 + \text{NH} \rightarrow \text{NH}_2 + \text{N}_2\text{H}_3$	1.00e+09	0.5	8.368	24
50	$\text{N}_2\text{H}_4 + \text{NH}_2 \rightarrow \text{N}_2\text{H}_3 + \text{NH}_3$	4.00e+07	0.5	8.368	43
51	$\text{N}_2\text{H}_4 + \text{N}_2\text{H}_2 \rightarrow \text{N}_2\text{H}_3 + \text{N}_2\text{H}_3$	2.50e+07	0.5	125.520	24

a) enhanced third-body coefficients $\text{H}_2=0.0$, b) enhanced third-body coefficients $\text{Ar}=0.2$, c) enhanced third body coefficients $\text{N}_2=2.0$, $\text{H}_2=2.0$, d) Rate constant in the high pressure limit, e) Rate constant in the low pressure limit

For reactions steps involving a third-body molecule the forward reaction rate (r_j^f) is given by

$$r_j^f = c_{mix} \times k_j^f \prod_i c_i^{v_i}$$

where c_i and v_i are the concentration and forward reaction coefficient for species i and c_{mix} is the enhanced total concentration

$$c_{mix} = \sum_i \gamma_i c_i$$

where the third-body coefficient γ_i for species i is unity if not otherwise specified. For reaction 44 (Table I) which is near the pressure fall-off limit the rate constant is given by the Lindemann formula⁴⁴

$$k = k_{\infty} \times \left(\frac{X}{1+X} \right)$$

where k_{∞} is the rate constant in the high-pressure limit and X is a reduced pressure given by $X = \frac{c_{mix}}{c_{lim}}$. c_{lim} is the fall-off pressure, which is given by $c_{lim} = \frac{k_{\infty}}{k_0}$ with k_0 being the rate constant in the low pressure limit.

Simulations were done at 100, 400, 700, 1000, 1300 and 1600 °C, 1, 10 and 100 mbar total pressure, an ammonia to carrier ratio of 1:100, 1:10 and 1:1 in four different carrier gasses; hydrogen gas (H₂), nitrogen gas (N₂), a mixture of equal amount hydrogen and nitrogen gas (50:50 H₂:N₂), and argon gas (Ar), yielding in total 216 parameter combinations, capturing the expected conditions during thermal CVD and atomic layer deposition (ALD) using ammonia. The simulations used the isothermal-isobaric ensemble with a batch reactor model fixing the temperature and pressure to the predetermined parameter value and letting the volume change by

$$dV = \frac{RT}{p} dn_{tot}. \quad (1)$$

All simulations studied the time-evolution of the amount of species during 120 seconds and started with only ammonia and carrier gas at $t = 0$ s.

For easier comparison, the degree of decomposition was calculated as the fraction of decomposed ammonia normalized by the initial amount of ammonia

$$\alpha_{NH_3} = \frac{n_{0,NH_3} - n_{t,NH_3}}{n_{0,NH_3}}. \quad (2)$$

By differentiating Eq. (2) with respect to time the decomposition rate is obtained, and that is used to investigate the decomposition profile of ammonia

$$\frac{d\alpha_{t,NH_3}}{dt} = -\frac{dn_{t,NH_3}}{dt} \times \frac{1}{n_{0,NH_3}}. \quad (3)$$

The decomposition rate Eq. (3) can also be obtained from the total reaction rate involving ammonia by

$$\frac{d\alpha_{t,NH_3}}{dt} = -\frac{V_t}{n_{0,NH_3}} \times \sum_j \nu_j (r_j^{fwd} - r_j^{rev}) \quad (4)$$

where r_j and ν_j is the rate and the net reaction coefficient of NH_3 for reaction j and V_t is the volume of the reactor at time t . Equation (4) gives a relation between the reaction rates and the decomposition rate and makes it possible to identify which reactions contribute the most to the decomposition.

III. RESULTS AND DISCUSSION

From the simulation the amounts and thereby the partial pressures of all species in the system were obtained. Figure 1a shows how the partial pressures relative to the initial pressure of ammonia evolve during 100 s at 1000 °C, 10 mbar total pressure and an ammonia to carrier ratio of 1:10 in all investigated carrier gases. The simulation shows that at these conditions ammonia is stable for a couple of seconds before any noticeable decomposition starts to occur in N_2 and Ar ambients and after 100 s only about 20 % of ammonia has decomposed, Fig. 1b. It can also be seen that when using a carrier

containing hydrogen gas, the decomposition decreases to almost zero. Less than 1 % of the ammonia has decomposed after 100 s in a pure hydrogen carrier gas.

FIG. 1. Ammonia decomposition as a function of time at 1000°C, 10 mbar and 1:10 ammonia to carrier ratio in different carrier gases. Solid lines denote H₂ as carrier, dashed lines N₂, dotted lines 50:50 H₂:N₂ and dash dotted lines Ar. (a) shows the gas phase composition and (b) shows the degree of decomposition of ammonia. In addition the thermodynamic equilibrium distribution is shown in the rightmost part of each figure.

The major decomposition products according to thermodynamics, N₂ and H₂, start to form after 0.5 s in N₂ and Ar. The N₂ and H₂ concentrations increase with time, but do

not reach the pressures expected at equilibrium during the simulated time 120 s. The most dominating decomposition intermediates in N_2 and Ar carriers are NH_2 and N_2H_2 . The abundance of N_2H_2 and absence of NH could be explained by NH forming dimers yielding N_2H_2 . These intermediates start to form quickly just before 1 s and reach their maximum pressures around 2 s, and then slowly deplete with time. For hydrogen-containing carriers the first significant intermediates showing up are hydrogen radicals, which become significant only after around 10 s.

The temperature dependence for the ammonia decomposition can be studied by comparing simulations at different temperatures. Figure S45 in the supplementary material²¹ shows the decomposition at 700 °C, 10 mbar and 1:10 ammonia to carrier ratio. At these conditions the decomposition is close to zero as seen by the almost unchanged pressures over the simulation time. Less than 2 ppm of the initial ammonia has decomposed in N_2 or Ar carriers after 100 s and even less in H_2 -containing carriers. If the temperature decreases even further, to 400 °C and 100 °C (Figs. S27 and S9), no decomposition of NH_3 is seen even after 100 s in all investigated carriers.

Ammonia is found to be more reactive at higher temperatures. Fig. 2 shows the decomposition at 1300 °C, 10 mbar and 1:10 ammonia to carrier ratio. Decomposition starts already at 100 ms in N_2 and Ar carriers. After 2-4 s half of the initial amount of ammonia has decomposed and over 95 % has decomposed after 100 s. After a few seconds the gas will be dominated by the major decomposition products, N_2 and H_2 , and the carriers. NH_3 shows much lower reactivity in H_2 -containing carriers compared to in N_2 and Ar also at 1300 °C with significant decomposition only occurring after around 10

s. NH_3 will reach 50 % decomposition in pure H_2 and 75 % decomposition in the H_2/N_2 mixture after 100 s.

FIG. 2. Ammonia decomposition as a function of time at 1300°C, 10 mbar and 1:10 ammonia to carrier ratio in different carrier gases. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 H_2/N_2 and dash dotted lines Ar. (a) shows the gas phase composition and (b) shows the degree of decomposition of ammonia. In addition the thermodynamic equilibrium distribution is shown in the rightmost part of each figure.

Similar to the 1000 °C simulation, at 1300 °C the major decomposition intermediates for decomposition in N_2 or Ar are NH_2 and N_2H_2 . Their maximum partial pressures are higher and are reached sooner at 1300 °C than at 1000 °C. The NH_2

concentration shows a plateau at its maximum pressure before it starts to decay at around 20 s. In pure H_2 and in the H_2/N_2 mixture the major decomposition product is NH_2 , but its partial pressure is significantly lower than in N_2 and Ar and it requires longer time for the partial pressure to become high enough to appear in the plot, i.e. around 0.1 s, significantly later than for in N_2 and Ar.

The trend of faster decomposition continues as the temperature is raised further to 1600 °C, Fig. S99. Decomposition starts even earlier and with slightly higher maximum pressures for the intermediates. Although the decomposition in hydrogen carriers is lower than for nitrogen or argon, the difference between the carriers is smaller than at lower temperature and in all carriers NH_3 decomposes fully before 10 s.

The dependence of the decomposition evolution on the total pressure was also investigated by comparing decomposition at different pressures, as seen in Figs. 1, S57 and S69. The partial pressure curves have very similar shapes with the same maxima regardless of total pressure. The main effect of changing pressure was a linear shift in degree of decomposition curve, by lowering the pressure by a factor 10, from 10 mbar to 1 mbar the decomposition occurred 10 times later (i.e. the degree of decomposition curves shifted to the right by a factor 10), as seen by comparing Figs. 1b and S57b. Instead by increasing the pressure to 100 mbar the decomposition occurred 10 times earlier (and should also enable equilibrium to be reached faster), see Figs. 1b and S69b.

By changing the ratio of ammonia to carrier, i.e. the initial partial pressure of ammonia, some changes in the time dependence of the decomposition occurs. As seen in Figs. S61, S63 and S65 the onset of decomposition is earlier for a high initial ammonia ratio; around 500 ms, 1 s and 5 s for 1:1, 1:10 and 1:100 ammonia to carrier ratio at 1000

°C, 10 mbar total pressure in nitrogen or argon carrier. It can be noticed that the degree of decomposition has a steeper slope when the ammonia to carrier ratio is low. The results also show that as the amount of carrier is decreased the decomposition profile becomes less dependent on the carrier type. This is expected as the main inhibitor for decomposition, hydrogen, is lowered if the amount of hydrogen-containing carrier is lowered.

FIG. 3. Forward (a), reverse (b) and net (c) reaction rate for all reactions involving NH_3 in the model and decomposition rate (d) as a function of time for 1000 °C, 10 mbar and 1:10 precursor to carrier ratio. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 H_2/N_2 and dash dotted lines Ar.

The evolution of the decomposition rate with time is shown in Fig. 3 and shows that the decomposition rate is much higher in nitrogen or argon than in hydrogen-containing carriers. The decomposition rate in nitrogen and argon follows the same profile; a tailing distribution with a sharp peak of maximum decomposition rate at approximately 2 s, with the main difference between N_2 and Ar being that the rate in nitrogen is slightly higher than in argon. The main contributing reaction for the ammonia decomposition is found to be the bimolecular decomposition assisted by a hydrogen radical (reaction 21, Table I) followed by dimerization with an already formed NH_2 (reaction 22, Table I). Both these reactions cannot start at time zero since no co-reactant is present, instead the processes start with bimolecular dissociation assisted by a third-body molecule (reactions 19 and 20, Table I). These reactions can then produce the needed intermediates to facilitate further decomposition.

Some of the reactions have very low reaction rates and most of these reactions contain species that have very low concentrations at the investigated conditions, such as the nitrogen radicals and the two dinitrogen species NNH and N_2H_4 . Although there are some differences in which reactions have the lowest reaction rate, five reactions stand out among the slowest at most conditions (i.e. reactions 51, 27, 26, 3 and 48 in Table I). If these reactions are omitted from the model, the differences in relative pressure and decomposition are not significant compared to if the reactions are included. The differences are somewhat larger when the overall reaction rate is higher, for example at high temperature or pressure, and care must therefore be taken if omitting these reactions.

Comparison of the net reaction rate in hydrogen-containing carriers with the net reaction rate in nitrogen or argon shows that the main decomposition pathway (reaction

21, Table I) is suppressed in hydrogen. The large amount of available hydrogen will result in reaction 21 having a high reverse rate, causing its equilibrium to be shifted towards ammonia, and thereby limiting the decomposition rate. As more hydrogen is decomposed into radicals, reaction 21 will start to dominate and be the main decomposition pathway, with reaction 22 being the second most important, which also is the dominant path in argon or nitrogen carriers.

IV. SUMMARY AND CONCLUSIONS

The decomposition of ammonia at CVD conditions was investigated by kinetic simulations, and it was found that at CVD and ALD conditions the decomposition of ammonia is limited by kinetics and does not reach equilibrium compositions during the expected residence time for gases in the reactors. This shows that an equilibrium model with almost full decomposition to dinitrogen and dihydrogen cannot be used alone to explain the low reactivity of ammonia in the growth processes. Instead the low reactivity is explained by the low concentration of the more reactive intermediates, e.g. NH_2 radicals, that could contribute to film growth. The simulations also show that hydrogen has a passivating effect on decomposition, mainly by reacting with the formed NH_2 radicals reforming ammonia before further reactions could occur. Lowering the amount of hydrogen in the carrier has the potential to increase the decomposition rate of ammonia to levels more suitable for film deposition.

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Supplementary material to Kinetic modeling of ammonia decomposition at CVD conditions

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1. Reverse reaction rate constants

The reverse reaction rate constants (k_r) for the reactions in the model were calculated via the forward rate constant (k_f) and equilibrium constant (K) by thermodynamic balance

$$k_r = \frac{k_f}{K \times \left(\frac{p_0}{RT}\right)^{\Delta n}}.$$

The equilibrium constant was calculated from NASA polynomials. Each species has two NASA polynomials, one for lower temperatures and one for higher. The coefficients and temperature ranges for the polynomials were obtained from the Chemkin Thermodynamic database¹ and are given in Table S1.

The polynomials are used to calculate enthalpy and entropy by

$$\frac{H}{RT} = a_1 + \frac{a_2 T}{2} + \frac{a_3 T^2}{3} + \frac{a_4 T^3}{4} + \frac{a_5 T^4}{5} + \frac{a_6}{T},$$
$$\frac{S}{R} = a_1 \ln \frac{T}{T_0} + a_2 T + \frac{a_3 T^2}{2} + \frac{a_4 T^3}{3} + \frac{a_5 T^4}{4} + a_7.$$

The equilibrium constant was then calculated from the reaction thermodynamics by

$$K = \exp\left(-\frac{\Delta_r H}{RT} + \frac{\Delta_r S}{R}\right).$$

¹ R.J. Kee, F.M. Rupley, and J.A. Miller, The Chemkin Thermodynamic Data Base, United States: N. p., 1990. Web.

Table S1. NASA polynomial coefficients and temperature ranges for all species in the model. Data obtained from Chemkin Thermodynamic database.

	T _{low} (K)	T _{high} (K)	a ₁	a ₂ (K ⁻¹)	a ₃ (K ⁻²)	a ₄ (K ⁻³)	a ₅ (K ⁻⁴)	a ₆ (K)	a ₇
NH3	1000.0	6000.0	0.26344521E+01	0.56662560E-02	-0.17278676E-05	0.23867161E-09	-0.12578786E-13	-0.65446958E+04	0.65662928E+01
	200.0	1000.0	0.42860274E+01	-0.46605230E-02	0.21718513E-04	-0.22808887E-07	0.82638046E-11	-0.67417285E+04	-0.62537277E+00
NH2	1000.0	6000.0	0.28347421E+01	0.32073082E-02	-0.93390804E-06	0.13702953E-09	-0.79206144E-14	0.22171957E+05	0.65204163E+01
	200.0	1000.0	0.42040029E+01	-0.21061385E-02	0.71068348E-05	-0.56115197E-08	0.16440717E-11	0.21885910E+05	-0.14184248E+00
NH	1000.0	6000.0	0.27836928E+01	0.13298430E-02	-0.42478047E-06	0.78348501E-10	-0.55044470E-14	0.42120848E+05	0.57407799E+01
	200.0	1000.0	0.34929085E+01	0.31179198E-03	-0.14890484E-05	0.24816442E-08	-0.10356967E-11	0.41880629E+05	0.18483278E+01
N	1000.0	6000.0	0.24159429E+01	0.17489065E-03	-0.11902369E-06	0.30226245E-10	-0.20360982E-14	0.56133773E+05	0.46496096E+01
	200.0	1000.0	0.25000000E+01	0.00000000E+00	0.00000000E+00	0.00000000E+00	0.00000000E+00	0.56104637E+05	0.41939087E+01
N2H4	1000.0	5000.0	0.04977317E+02	0.09595519E-01	-0.03547639E-04	0.06124299E-08	-0.04029795E-12	0.09341219E+05	-0.02962989E+02
	300.0	1000.0	0.06442605E+00	0.02749729E+00	-0.02899451E-03	0.01745239E-06	-0.04422282E-10	0.10451917E+05	0.02127789E+03
N2H3	1000.0	5000.0	0.04441846E+02	0.07214270E-01	-0.02495684E-04	0.03920564E-08	-0.02298949E-12	0.16642211E+05	-0.04275204E+01
	300.0	1000.0	0.03174203E+02	0.04715907E-01	0.13348671E-04	-0.01919684E-06	0.07487563E-10	0.01727269E+06	0.07557224E+02
N2H2	1000.0	5000.0	0.03371185E+02	0.06039968E-01	-0.02303853E-04	0.04062789E-08	-0.02713144E-12	0.02418172E+06	0.04980585E+02
	300.0	1000.0	0.16179994E+01	0.13063122E-01	-0.01715711E-03	0.16056079E-07	-0.06093638E-10	0.02467526E+06	0.13794670E+02
NNH	1000.0	6000.0	0.37667544E+01	0.28915082E-02	-0.10416620E-05	0.16842594E-09	-0.10091896E-13	0.28650697E+05	0.44705067E+01
	200.0	1000.0	0.43446927E+01	-0.48497072E-02	0.20059459E-04	-0.21726464E-07	0.79469539E-11	0.28791973E+05	0.29779410E+01
N2	1000.0	5000.0	0.02926640E+02	0.14879768E-02	-0.05684760E-05	0.10097038E-09	-0.06753351E-13	-0.09227977E+04	0.05980528E+02
	300.0	1000.0	0.03298677E+02	0.14082404E-02	-0.03963222E-04	0.05641515E-07	-0.02444854E-10	-0.10208999E+04	0.03950372E+02
H2	1000.0	3500.0	3.33727920E+00	-4.94024731E-05	4.99456778E-07	-1.79566394E-10	2.00255376E-14	-9.50158922E+02	-3.20502331E+00
	200.0	1000.0	2.34433112E+00	7.98052075E-03	-1.94781510E-05	2.01572094E-08	-7.37611761E-12	-9.17935173E+02	6.83010238E-01
H	1000.0	3500.0	2.50000001E+00	-2.30842973E-11	1.61561948E-14	-4.73515235E-18	4.98197357E-22	2.54736599E+04	-4.46682914E-01
	200.0	1000.0	2.50000000E+00	7.05332819E-13	-1.99591964E-15	2.30081632E-18	-9.27732332E-22	2.54736599E+04	-4.46682853E-01
Ar	1000.0	5000.0	0.02500000E+02	0.00000000E+00	0.00000000E+00	0.00000000E+00	0.00000000E+00	-0.07453750E+04	0.04366000E+02
	300.0	1000.0	0.02500000E+02	0.00000000E+00	0.00000000E+00	0.00000000E+00	0.00000000E+00	-0.07453750E+04	0.04366000E+02

2. Simulation results

The following figures (Figure S1-S108) contains the results from simulations of ammonia decomposition in Ar, N₂, H₂ and 50:50 H₂:N₂ carrier gasses at all parameter combinations. The figures are ordered according to temperature, Figure S1-S18 depicts simulations at 100 °C, Figure S19-S36 at 400 °C, Figure S37-S54 at 700 °C, Figure S55-S72 at 1000 °C, Figure S73-S90 at 1300 °C and Figure S91-S108 at 1600 °C. At each temperature, the figures are sorted firstly by increasing total pressure (1 mbar, 10 mbar and 100 mbar) and then by decreasing NH₃ concentration (1:1, 1:10 and 1:100). Odd numbered figures depict the gas phase composition and the degree of decomposition of NH₃ while the even numbered show the reaction and decomposition rates (Eqs. 3-4).

Figure S1. Ammonia decomposition at 100 °C, 1 mbar and 1:1 ammonia to carrier ratio in different carrier gases. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar. (a) shows the gas phase composition and (b) shows the degree of decomposition of ammonia.

Figure S2. Forward (a), reverse (b) and net (c) reaction rate for all reactions involving NH_3 in the model and decomposition rate (d) for 100 °C, 1 mbar and 1:1 precursor to carrier ratio. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar.

Figure S3. Ammonia decomposition at 100 °C, 1 mbar and 1:10 ammonia to carrier ratio in different carrier gases. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar. (a) shows the gas phase composition and (b) shows the degree of decomposition of ammonia.

Figure S4. Forward (a), reverse (b) and net (c) reaction rate for all reactions involving NH_3 in the model and decomposition rate (d) for 100 °C, 1 mbar and 1:10 precursor to carrier ratio. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar.

Figure S5. Ammonia decomposition at 100 °C, 1 mbar and 1:100 ammonia to carrier ratio in different carrier gases. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar. (a) shows the gas phase composition and (b) shows the degree of decomposition of ammonia.

Figure S6. Forward (a), reverse (b) and net (c) reaction rate for all reactions involving NH_3 in the model and decomposition rate (d) for 100 °C, 1 mbar and 1:100 precursor to carrier ratio. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar.

Figure S7. Ammonia decomposition at 100 °C, 10 mbar and 1:1 ammonia to carrier ratio in different carrier gases. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar. (a) shows the gas phase composition and (b) shows the degree of decomposition of ammonia.

Figure S8. Forward (a), reverse (b) and net (c) reaction rate for all reactions involving NH_3 in the model and decomposition rate (d) for 100 °C, 10 mbar and 1:1 precursor to carrier ratio. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar.

Figure S9. Ammonia decomposition at 100 °C, 10 mbar and 1:10 ammonia to carrier ratio in different carrier gases. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar. (a) shows the gas phase composition and (b) shows the degree of decomposition of ammonia.

Figure S10. Forward (a), reverse (b) and net (c) reaction rate for all reactions involving NH_3 in the model and decomposition rate (d) for 100 °C, 10 mbar and 1:10 precursor to carrier ratio. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar.

Figure S11. Ammonia decomposition at 100 °C, 10 mbar and 1:100 ammonia to carrier ratio in different carrier gases. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar . (a) shows the gas phase composition and (b) shows the degree of decomposition of ammonia.

Figure S12. Forward (a), reverse (b) and net (c) reaction rate for all reactions involving NH_3 in the model and decomposition rate (d) for 100 °C, 10 mbar and 1:100 precursor to carrier ratio. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar .

Figure S13. Ammonia decomposition at 100 °C, 100 mbar and 1:1 ammonia to carrier ratio in different carrier gases. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $H_2:N_2$ and dash dotted lines Ar. (a) shows the gas phase composition and (b) shows the degree of decomposition of ammonia.

Figure S14. Forward (a), reverse (b) and net (c) reaction rate for all reactions involving NH_3 in the model and decomposition rate (d) for 100 °C, 100 mbar and 1:1 precursor to carrier ratio. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $H_2:N_2$ and dash dotted lines Ar.

Figure S15. Ammonia decomposition at 100 °C, 100 mbar and 1:10 ammonia to carrier ratio in different carrier gases. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar. (a) shows the gas phase composition and (b) shows the degree of decomposition of ammonia.

Figure S16. Forward (a), reverse (b) and net (c) reaction rate for all reactions involving NH_3 in the model and decomposition rate (d) for 100 °C, 100 mbar and 1:10 precursor to carrier ratio. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar.

Figure S17. Ammonia decomposition at 100 °C, 100 mbar and 1:100 ammonia to carrier ratio in different carrier gases. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar. (a) shows the gas phase composition and (b) shows the degree of decomposition of ammonia.

Figure S18. Forward (a), reverse (b) and net (c) reaction rate for all reactions involving NH_3 in the model and decomposition rate (d) for 100 °C, 100 mbar and 1:100 precursor to carrier ratio. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar.

Figure S19. Ammonia decomposition at 400 °C, 1 mbar and 1:1 ammonia to carrier ratio in different carrier gases. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar . (a) shows the gas phase composition and (b) shows the degree of decomposition of ammonia.

Figure S20. Forward (a), reverse (b) and net (c) reaction rate for all reactions involving NH_3 in the model and decomposition rate (d) for 400 °C, 1 mbar and 1:1 precursor to carrier ratio. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar .

Figure S21. Ammonia decomposition at 400 °C, 1 mbar and 1:10 ammonia to carrier ratio in different carrier gases. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar. (a) shows the gas phase composition and (b) shows the degree of decomposition of ammonia.

Figure S22. Forward (a), reverse (b) and net (c) reaction rate for all reactions involving NH_3 in the model and decomposition rate (d) for 400 °C, 1 mbar and 1:10 precursor to carrier ratio. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar.

Figure S23. Ammonia decomposition at 400 °C, 1 mbar and 1:100 ammonia to carrier ratio in different carrier gases. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar . (a) shows the gas phase composition and (b) shows the degree of decomposition of ammonia.

Figure S24. Forward (a), reverse (b) and net (c) reaction rate for all reactions involving NH_3 in the model and decomposition rate (d) for 400 °C, 1 mbar and 1:100 precursor to carrier ratio. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar .

Figure S25. Ammonia decomposition at 400 °C, 10 mbar and 1:1 ammonia to carrier ratio in different carrier gases. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar . (a) shows the gas phase composition and (b) shows the degree of decomposition of ammonia.

Figure S26. Forward (a), reverse (b) and net (c) reaction rate for all reactions involving NH_3 in the model and decomposition rate (d) for 400 °C, 10 mbar and 1:1 precursor to carrier ratio. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar .

Figure S27. Ammonia decomposition at 400 °C, 10 mbar and 1:10 ammonia to carrier ratio in different carrier gases. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar. (a) shows the gas phase composition and (b) shows the degree of decomposition of ammonia.

Figure S28. Forward (a), reverse (b) and net (c) reaction rate for all reactions involving NH_3 in the model and decomposition rate (d) for 400 °C, 10 mbar and 1:10 precursor to carrier ratio. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar.

Figure S29. Ammonia decomposition at 400 °C, 10 mbar and 1:100 ammonia to carrier ratio in different carrier gases. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar. (a) shows the gas phase composition and (b) shows the degree of decomposition of ammonia.

Figure S30. Forward (a), reverse (b) and net (c) reaction rate for all reactions involving NH_3 in the model and decomposition rate (d) for 400 °C, 10 mbar and 1:100 precursor to carrier ratio. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar.

Figure S31. Ammonia decomposition at 400 °C, 100 mbar and 1:1 ammonia to carrier ratio in different carrier gases. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar. (a) shows the gas phase composition and (b) shows the degree of decomposition of ammonia.

Figure S32. Forward (a), reverse (b) and net (c) reaction rate for all reactions involving NH_3 in the model and decomposition rate (d) for 400 °C, 100 mbar and 1:1 precursor to carrier ratio. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar.

Figure S33. Ammonia decomposition at 400 °C, 100 mbar and 1:10 ammonia to carrier ratio in different carrier gases. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar. (a) shows the gas phase composition and (b) shows the degree of decomposition of ammonia.

Figure S34. Forward (a), reverse (b) and net (c) reaction rate for all reactions involving NH_3 in the model and decomposition rate (d) for 400 °C, 100 mbar and 1:10 precursor to carrier ratio. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar.

Figure S35. Ammonia decomposition at 400 °C, 100 mbar and 1:100 ammonia to carrier ratio in different carrier gases. Solid lines denote H₂ as carrier, dashed lines N₂, dotted lines 50:50 H₂:N₂ and dash dotted lines Ar. (a) shows the gas phase composition and (b) shows the degree of decomposition of ammonia.

Figure S36. Forward (a), reverse (b) and net (c) reaction rate for all reactions involving NH₃ in the model and decomposition rate (d) for 400 °C, 100 mbar and 1:100 precursor to carrier ratio. Solid lines denote H₂ as carrier, dashed lines N₂, dotted lines 50:50 H₂:N₂ and dash dotted lines Ar.

Figure S37. Ammonia decomposition at 700 °C, 1 mbar and 1:1 ammonia to carrier ratio in different carrier gases. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar . (a) shows the gas phase composition and (b) shows the degree of decomposition of ammonia.

Figure S38. Forward (a), reverse (b) and net (c) reaction rate for all reactions involving NH_3 in the model and decomposition rate (d) for 700 °C, 1 mbar and 1:1 precursor to carrier ratio. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar .

Figure S39. Ammonia decomposition at 700 °C, 1 mbar and 1:10 ammonia to carrier ratio in different carrier gases. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar . (a) shows the gas phase composition and (b) shows the degree of decomposition of ammonia.

Figure S40. Forward (a), reverse (b) and net (c) reaction rate for all reactions involving NH_3 in the model and decomposition rate (d) for 700 °C, 1 mbar and 1:10 precursor to carrier ratio. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar .

Figure S41. Ammonia decomposition at 700 °C, 1 mbar and 1:100 ammonia to carrier ratio in different carrier gases. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar. (a) shows the gas phase composition and (b) shows the degree of decomposition of ammonia.

Figure S42. Forward (a), reverse (b) and net (c) reaction rate for all reactions involving NH_3 in the model and decomposition rate (d) for 700 °C, 1 mbar and 1:100 precursor to carrier ratio. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar.

Figure S43. Ammonia decomposition at 700 °C, 10 mbar and 1:1 ammonia to carrier ratio in different carrier gases. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar . (a) shows the gas phase composition and (b) shows the degree of decomposition of ammonia.

Figure S44. Forward (a), reverse (b) and net (c) reaction rate for all reactions involving NH_3 in the model and decomposition rate (d) for 700 °C, 10 mbar and 1:1 precursor to carrier ratio. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar .

Figure S45. Ammonia decomposition at 700 °C, 10 mbar and 1:10 ammonia to carrier ratio in different carrier gases. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar . (a) shows the gas phase composition and (b) shows the degree of decomposition of ammonia.

Figure S46. Forward (a), reverse (b) and net (c) reaction rate for all reactions involving NH_3 in the model and decomposition rate (d) for 700 °C, 10 mbar and 1:10 precursor to carrier ratio. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar .

Figure S47. Ammonia decomposition at 700 °C, 10 mbar and 1:100 ammonia to carrier ratio in different carrier gases. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar . (a) shows the gas phase composition and (b) shows the degree of decomposition of ammonia.

Figure S48. Forward (a), reverse (b) and net (c) reaction rate for all reactions involving NH_3 in the model and decomposition rate (d) for 700 °C, 10 mbar and 1:100 precursor to carrier ratio. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar .

Figure S49. Ammonia decomposition at 700 °C, 100 mbar and 1:1 ammonia to carrier ratio in different carrier gases. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar . (a) shows the gas phase composition and (b) shows the degree of decomposition of ammonia.

Figure S50. Forward (a), reverse (b) and net (c) reaction rate for all reactions involving NH_3 in the model and decomposition rate (d) for 700 °C, 100 mbar and 1:1 precursor to carrier ratio. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar .

Figure S51. Ammonia decomposition at 700 °C, 100 mbar and 1:10 ammonia to carrier ratio in different carrier gases. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2\text{:N}_2$ and dash dotted lines Ar. (a) shows the gas phase composition and (b) shows the degree of decomposition of ammonia.

Figure S52. Forward (a), reverse (b) and net (c) reaction rate for all reactions involving NH_3 in the model and decomposition rate (d) for 700 °C, 100 mbar and 1:10 precursor to carrier ratio. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2\text{:N}_2$ and dash dotted lines Ar.

Figure S53. Ammonia decomposition at 700 °C, 100 mbar and 1:100 ammonia to carrier ratio in different carrier gases. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2\text{:N}_2$ and dash dotted lines Ar. (a) shows the gas phase composition and (b) shows the degree of decomposition of ammonia.

Figure S54. Forward (a), reverse (b) and net (c) reaction rate for all reactions involving NH_3 in the model and decomposition rate (d) for 700 °C, 100 mbar and 1:100 precursor to carrier ratio. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2\text{:N}_2$ and dash dotted lines Ar.

Figure S55. Ammonia decomposition at 1000 °C, 1 mbar and 1:1 ammonia to carrier ratio in different carrier gases. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar. (a) shows the gas phase composition and (b) shows the degree of decomposition of ammonia.

Figure S56. Forward (a), reverse (b) and net (c) reaction rate for all reactions involving NH_3 in the model and decomposition rate (d) for 1000 °C, 1 mbar and 1:1 precursor to carrier ratio. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar.

Figure S57. Ammonia decomposition at 1000 °C, 1 mbar and 1:10 ammonia to carrier ratio in different carrier gases. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar. (a) shows the gas phase composition and (b) shows the degree of decomposition of ammonia.

Figure S58. Forward (a), reverse (b) and net (c) reaction rate for all reactions involving NH_3 in the model and decomposition rate (d) for 1000 °C, 1 mbar and 1:10 precursor to carrier ratio. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar.

Figure S59. Ammonia decomposition at 1000 °C, 1 mbar and 1:100 ammonia to carrier ratio in different carrier gases. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar . (a) shows the gas phase composition and (b) shows the degree of decomposition of ammonia.

Figure S60. Forward (a), reverse (b) and net (c) reaction rate for all reactions involving NH_3 in the model and decomposition rate (d) for 1000 °C, 1 mbar and 1:100 precursor to carrier ratio. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar .

Figure S61. Ammonia decomposition at 1000 °C, 10 mbar and 1:1 ammonia to carrier ratio in different carrier gases. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 H_2 : N_2 and dash dotted lines Ar . (a) shows the gas phase composition and (b) shows the degree of decomposition of ammonia.

Figure S62. Forward (a), reverse (b) and net (c) reaction rate for all reactions involving NH_3 in the model and decomposition rate (d) for 1000 °C, 10 mbar and 1:1 precursor to carrier ratio. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 H_2 : N_2 and dash dotted lines Ar .

Figure S63. Ammonia decomposition at 1000 °C, 10 mbar and 1:10 ammonia to carrier ratio in different carrier gases. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar . (a) shows the gas phase composition and (b) shows the degree of decomposition of ammonia.

Figure S64. Forward (a), reverse (b) and net (c) reaction rate for all reactions involving NH_3 in the model and decomposition rate (d) for 1000 °C, 10 mbar and 1:10 precursor to carrier ratio. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar .

Figure S65. Ammonia decomposition at 1000 °C, 10 mbar and 1:100 ammonia to carrier ratio in different carrier gases. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2\text{:N}_2$ and dash dotted lines Ar . (a) shows the gas phase composition and (b) shows the degree of decomposition of ammonia.

Figure S66. Forward (a), reverse (b) and net (c) reaction rate for all reactions involving NH_3 in the model and decomposition rate (d) for 1000 °C, 10 mbar and 1:100 precursor to carrier ratio. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2\text{:N}_2$ and dash dotted lines Ar .

Figure S67. Ammonia decomposition at 1000 °C, 100 mbar and 1:1 ammonia to carrier ratio in different carrier gases. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar. (a) shows the gas phase composition and (b) shows the degree of decomposition of ammonia.

Figure S68. Forward (a), reverse (b) and net (c) reaction rate for all reactions involving NH_3 in the model and decomposition rate (d) for 1000 °C, 100 mbar and 1:1 precursor to carrier ratio. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar.

Figure S69. Ammonia decomposition at 1000 °C, 100 mbar and 1:10 ammonia to carrier ratio in different carrier gases. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 H_2 : N_2 and dash dotted lines Ar. (a) shows the gas phase composition and (b) shows the degree of decomposition of ammonia.

Figure S70. Forward (a), reverse (b) and net (c) reaction rate for all reactions involving NH_3 in the model and decomposition rate (d) for 1000 °C, 100 mbar and 1:10 precursor to carrier ratio. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 H_2 : N_2 and dash dotted lines Ar.

Figure S71. Ammonia decomposition at 1000 °C, 100 mbar and 1:100 ammonia to carrier ratio in different carrier gases. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 H_2 : N_2 and dash dotted lines Ar. (a) shows the gas phase composition and (b) shows the degree of decomposition of ammonia.

Figure S72. Forward (a), reverse (b) and net (c) reaction rate for all reactions involving NH_3 in the model and decomposition rate (d) for 1000 °C, 100 mbar and 1:100 precursor to carrier ratio. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 H_2 : N_2 and dash dotted lines Ar.

Figure S73. Ammonia decomposition at 1300 °C, 1 mbar and 1:1 ammonia to carrier ratio in different carrier gases. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar. (a) shows the gas phase composition and (b) shows the degree of decomposition of ammonia.

Figure S74. Forward (a), reverse (b) and net (c) reaction rate for all reactions involving NH_3 in the model and decomposition rate (d) for 1300 °C, 1 mbar and 1:1 precursor to carrier ratio. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar.

Figure S75. Ammonia decomposition at 1300 °C, 1 mbar and 1:10 ammonia to carrier ratio in different carrier gases. Solid lines denote H₂ as carrier, dashed lines N₂, dotted lines 50:50 H₂:N₂ and dash dotted lines Ar. (a) shows the gas phase composition and (b) shows the degree of decomposition of ammonia.

Figure S76. Forward (a), reverse (b) and net (c) reaction rate for all reactions involving NH₃ in the model and decomposition rate (d) for 1300 °C, 1 mbar and 1:10 precursor to carrier ratio. Solid lines denote H₂ as carrier, dashed lines N₂, dotted lines 50:50 H₂:N₂ and dash dotted lines Ar.

Figure S77. Ammonia decomposition at 1300 °C, 1 mbar and 1:100 ammonia to carrier ratio in different carrier gases. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 H_2 : N_2 and dash dotted lines Ar. (a) shows the gas phase composition and (b) shows the degree of decomposition of ammonia.

Figure S78. Forward (a), reverse (b) and net (c) reaction rate for all reactions involving NH_3 in the model and decomposition rate (d) for 1300 °C, 1 mbar and 1:100 precursor to carrier ratio. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 H_2 : N_2 and dash dotted lines Ar.

Figure S79. Ammonia decomposition at 1300 °C, 10 mbar and 1:1 ammonia to carrier ratio in different carrier gases. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar. (a) shows the gas phase composition and (b) shows the degree of decomposition of ammonia.

Figure S80. Forward (a), reverse (b) and net (c) reaction rate for all reactions involving NH_3 in the model and decomposition rate (d) for 1300 °C, 10 mbar and 1:1 precursor to carrier ratio. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar.

Figure S81. Ammonia decomposition at 1300 °C, 10 mbar and 1:10 ammonia to carrier ratio in different carrier gases. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar. (a) shows the gas phase composition and (b) shows the degree of decomposition of ammonia.

Figure S82. Forward (a), reverse (b) and net (c) reaction rate for all reactions involving NH_3 in the model and decomposition rate (d) for 1300 °C, 10 mbar and 1:10 precursor to carrier ratio. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar.

Figure S83. Ammonia decomposition at 1300 °C, 10 mbar and 1:100 ammonia to carrier ratio in different carrier gases. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar . (a) shows the gas phase composition and (b) shows the degree of decomposition of ammonia.

Figure S84. Forward (a), reverse (b) and net (c) reaction rate for all reactions involving NH_3 in the model and decomposition rate (d) for 1300 °C, 10 mbar and 1:100 precursor to carrier ratio. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar .

Figure S85. Ammonia decomposition at 1300 °C, 100 mbar and 1:1 ammonia to carrier ratio in different carrier gases. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar . (a) shows the gas phase composition and (b) shows the degree of decomposition of ammonia.

Figure S86. Forward (a), reverse (b) and net (c) reaction rate for all reactions involving NH_3 in the model and decomposition rate (d) for 1300 °C, 100 mbar and 1:1 precursor to carrier ratio. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar .

Figure S87. Ammonia decomposition at 1300 °C, 100 mbar and 1:10 ammonia to carrier ratio in different carrier gases. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar . (a) shows the gas phase composition and (b) shows the degree of decomposition of ammonia.

Figure S88. Forward (a), reverse (b) and net (c) reaction rate for all reactions involving NH_3 in the model and decomposition rate (d) for 1300 °C, 100 mbar and 1:10 precursor to carrier ratio. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar .

Figure S89. Ammonia decomposition at 1300 °C, 100 mbar and 1:100 ammonia to carrier ratio in different carrier gases. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar. (a) shows the gas phase composition and (b) shows the degree of decomposition of ammonia.

Figure S90. Forward (a), reverse (b) and net (c) reaction rate for all reactions involving NH_3 in the model and decomposition rate (d) for 1300 °C, 100 mbar and 1:100 precursor to carrier ratio. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar.

Figure S91. Ammonia decomposition at 1600 °C, 1 mbar and 1:1 ammonia to carrier ratio in different carrier gases. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar . (a) shows the gas phase composition and (b) shows the degree of decomposition of ammonia.

Figure S92. Forward (a), reverse (b) and net (c) reaction rate for all reactions involving NH_3 in the model and decomposition rate (d) for 1600 °C, 1 mbar and 1:1 precursor to carrier ratio. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar .

Figure S93. Ammonia decomposition at 1600 °C, 1 mbar and 1:10 ammonia to carrier ratio in different carrier gases. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar. (a) shows the gas phase composition and (b) shows the degree of decomposition of ammonia.

Figure S94. Forward (a), reverse (b) and net (c) reaction rate for all reactions involving NH_3 in the model and decomposition rate (d) for 1600 °C, 1 mbar and 1:10 precursor to carrier ratio. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar.

Figure S95. Ammonia decomposition at 1600 °C, 1 mbar and 1:100 ammonia to carrier ratio in different carrier gases. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar. (a) shows the gas phase composition and (b) shows the degree of decomposition of ammonia.

Figure S96. Forward (a), reverse (b) and net (c) reaction rate for all reactions involving NH_3 in the model and decomposition rate (d) for 1600 °C, 1 mbar and 1:100 precursor to carrier ratio. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar.

Figure S97. Ammonia decomposition at 1600 °C, 10 mbar and 1:1 ammonia to carrier ratio in different carrier gases. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar . (a) shows the gas phase composition and (b) shows the degree of decomposition of ammonia.

Figure S98. Forward (a), reverse (b) and net (c) reaction rate for all reactions involving NH_3 in the model and decomposition rate (d) for 1600 °C, 10 mbar and 1:1 precursor to carrier ratio. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar .

Figure S99. Ammonia decomposition at 1600 °C, 10 mbar and 1:10 ammonia to carrier ratio in different carrier gases. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar. (a) shows the gas phase composition and (b) shows the degree of decomposition of ammonia.

Figure S100. Forward (a), reverse (b) and net (c) reaction rate for all reactions involving NH_3 in the model and decomposition rate (d) for 1600 °C, 10 mbar and 1:10 precursor to carrier ratio. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar.

Figure S101. Ammonia decomposition at 1600 °C, 10 mbar and 1:100 ammonia to carrier ratio in different carrier gases. Solid lines denote H₂ as carrier, dashed lines N₂, dotted lines 50:50 H₂:N₂ and dash dotted lines Ar. (a) shows the gas phase composition and (b) shows the degree of decomposition of ammonia.

Figure S102. Forward (a), reverse (b) and net (c) reaction rate for all reactions involving NH₃ in the model and decomposition rate (d) for 1600 °C, 10 mbar and 1:100 precursor to carrier ratio. Solid lines denote H₂ as carrier, dashed lines N₂, dotted lines 50:50 H₂:N₂ and dash dotted lines Ar.

Figure S103. Ammonia decomposition at 1600 °C, 100 mbar and 1:1 ammonia to carrier ratio in different carrier gases. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar. (a) shows the gas phase composition and (b) shows the degree of decomposition of ammonia.

Figure S104. Forward (a), reverse (b) and net (c) reaction rate for all reactions involving NH_3 in the model and decomposition rate (d) for 1600 °C, 100 mbar and 1:1 precursor to carrier ratio. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar.

Figure S105. Ammonia decomposition at 1600 °C, 100 mbar and 1:10 ammonia to carrier ratio in different carrier gases. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar. (a) shows the gas phase composition and (b) shows the degree of decomposition of ammonia.

Figure S106. Forward (a), reverse (b) and net (c) reaction rate for all reactions involving NH_3 in the model and decomposition rate (d) for 1600 °C, 100 mbar and 1:10 precursor to carrier ratio. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar.

Figure S107. Ammonia decomposition at 1600 °C, 100 mbar and 1:100 ammonia to carrier ratio in different carrier gases. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar . (a) shows the gas phase composition and (b) shows the degree of decomposition of ammonia.

Figure S108. Forward (a), reverse (b) and net (c) reaction rate for all reactions involving NH_3 in the model and decomposition rate (d) for 1600 °C, 100 mbar and 1:100 precursor to carrier ratio. Solid lines denote H_2 as carrier, dashed lines N_2 , dotted lines 50:50 $\text{H}_2:\text{N}_2$ and dash dotted lines Ar .