Detailed study of the plasma-activated catalytic generation of ammonia in N₂-H₂ plasmas

Citation for published version (APA):

Helden, van, J. H., Wagemans, W., Yagci, G., Zijlmans, R. A. B., Schram, D. C., Engeln, R. A. H., Lombardi, G., Stancu, G. D., & Roepcke, J. (2007). Detailed study of the plasma-activated catalytic generation of ammonia in N₂-H₂ plasmas. *Journal of Applied Physics*, 101(4), 043305-1/12. [043305]. <https://doi.org/10.1063/1.2645828>

DOI:

[10.1063/1.2645828](https://doi.org/10.1063/1.2645828)

Document status and date:

Published: 01/01/2007

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

Detailed study of the plasma-activated catalytic generation of ammonia in N_2 - H_2 plasmas

J. H. van Helden, W. Wagemans, G. Yagci, R. A. B. Zijlmans, D. C. Schram, and R. Engeln^{a)}

Department of Applied Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB, Eindhoven, The Netherlands

G. Lombardi,^{b)} G. D. Stancu, and J. Röpcke

Institut für Niedertemperatur-Plasmaphysik, Friedrich-Ludwig-Jahn-Strasse 19, 17489 Greifswald, Germany

(Received 25 September 2006; accepted 1 January 2007; published online 27 February 2007; publisher error corrected 28 February 2007)

We investigated the efficiency and formation mechanism of ammonia generation in recombining plasmas generated from mixtures of N_2 and H_2 under various plasma conditions. In contrast to the Haber-Bosch process, in which the molecules are dissociated on a catalytic surface, under these plasma conditions the precursor molecules, N_2 and H_2 , are already dissociated in the gas phase. Surfaces are thus exposed to large fluxes of atomic N and H radicals. The ammonia production turns out to be strongly dependent on the fluxes of atomic N and H radicals to the surface. By optimizing the atomic N and H fluxes to the surface using an atomic nitrogen and hydrogen source ammonia can be formed efficiently, i.e., more than 10% of the total background pressure is measured to be ammonia. The results obtained show a strong similarity with results reported in literature, which were explained by the production of ammonia at the surface by stepwise addition reactions between adsorbed nitrogen and hydrogen containing radicals at the surface and incoming N and H containing radicals. Furthermore, our results indicate that the ammonia production is independent of wall material. The high fluxes of N and H radicals in our experiments result in a passivated surface, and the actual chemistry, leading to the formation of ammonia, takes place in an additional layer on top of this passivated surface. © 2007 American Institute of Physics. [DOI: 10.1063/1.2645828]

I. INTRODUCTION

The synthesis of ammonia from nitrogen and hydrogen gas on iron catalysts, known as the Haber-Bosch process, is considered as one of the most important discoveries in the history of industrial catalysis¹ and has often been called the most important invention of the 20th century.² Today, the artificial fertilizer produced with the Haber-Bosch process is responsible for sustaining roughly 40% of the Earth's population.³ To fully understand the processes on the surface leading to ammonia and to increase its efficiency, e.g., by using other catalysts like ruthenium,^{4,5} even today the process of ammonia synthesis is investigated.

The mechanism that is generally accepted for the ammonia production is the following: dissociative chemisorption of N_2 is followed by stepwise recombination of chemisorbed atomic nitrogen and hydrogen to NH_3 at the surface of the catalyst with NH and NH_2 as reaction intermediates.^{6,7} The rate-limiting step in the ammonia synthesis is the dissociative chemisorption of N_2 molecules on the surface of the catalyst, due to the very high binding energy of 9.6 eV of N_2 .

Nomura *et al.*⁸ suggested that excited N_2 molecules would improve the dissociative adsorption of N_2 . The lowest excited state of N_2 , the $A^3\Sigma_u^+$ state, lies at 6.2 eV; then, only

3.4 eV is necessary to dissociate the nitrogen molecule. The production of excited N_2 or even direct production of N atoms can be achieved by plasma and then other catalysts than iron or ruthenium may be used to enhance the ammonia production.

In 1971, Eremin *et al.*⁹ showed that the synthesis of ammonia in mixtures of nitrogen and hydrogen in a barrier discharge was increased by a factor of 1.5 to 4 when, respectively, copper, nickel, iron, or platinum wires were wound on the inner electrode of the reactor. It was shown by various research groups that ammonia production using plasmas is dependent on the type of wall material (up to a factor of 3).¹⁰⁻¹³ The wall is namely still used as a catalyst to form adsorbed nitrogen atoms by the dissociative adsorption of excited N_2 molecules or molecular nitrogen ions. In 1989, Uyama and Matsumoto reported that zeolite added to the downstream plasma in high-frequency discharges facilitated the ammonia production. This enhancement can at least partly be ascribed to a change in effective surface area. The ammonia production was ascribed to the surface reaction of NH_x radicals adsorbed on the zeolite with hydrogen atoms.¹⁴ The formation of ammonia in plasmas is still not completely understood but it is assumed that plasma-surface interactions play an important role. The formation of ammonia is generally ascribed to stepwise addition reactions between adsorbed nitrogen and hydrogen containing radicals at the surface and incoming N and H containing radicals.¹⁵⁻¹⁸

To gain a better understanding of plasma-surface inter-

^{a)}Author to whom correspondence should be addressed; Electronic mail: r.engeln@tue.nl

^{b)}Present address: LIMHP, CNRS-UPR 1311, Université Paris 13, 99 Avenue J. B. Clément, 93430 Villetaneuse, France.

actions that take place during the generation of stable molecules, we have chosen to investigate the formation of ammonia in plasmas of mixtures of nitrogen and hydrogen in more detail. Plasmas containing nitrogen and hydrogen are also extensively studied because of their widespread applications in research and industrial environments. The plasmas are used for the chemical synthesis of ammonia,^{9,11,14} nitriding of materials,¹⁷ the deposition of amorphous silicon nitride ($a\text{-SiN}_x\text{:H}$) films for solar cell applications,¹⁹ the plasma-assisted atomic layer deposition of TiN thin films,²⁰ and the etching of organic low k films.²¹

Previously, we have shown that ammonia can be formed efficiently in plasmas generated from mixtures of nitrogen and hydrogen via plasma-activated catalysis.²² In this article, we present a detailed study of the plasma-activated catalytic generation of ammonia in recombining plasmas generated from mixtures of N_2 and H_2 with the remote expanding thermal plasma (ETP) technique.²³ In the experiments, the plasma is used to dissociate the precursor molecules already before they come in contact with a surface. Then, the surface is exposed to fluxes of atomic and molecular radicals rather than molecules. The (passivated) surface of the plasma reactor, i.e., a surface covered by atomic and/or molecular radicals, acts as a catalyst. The process is called plasma-activated catalysis.²² We note that in our experiments, the N and H radicals are already produced in the plasma and as a result the flux of N and H radicals to the surface is up to $10^{21} \text{ m}^{-2} \text{ s}^{-1}$,^{24–26} which is at least one order of magnitude higher than in previous experiments in which plasma was used (see, e.g., Ref. 12). In the present experiments, the fluxes of radicals at the surface of the vessel are several tens of monolayers per second.

In this study, fluxes of hydrogen and nitrogen radicals are produced in a high-density plasma source with high dissociation degree. This plasma expands into a low-pressure vessel, where most of the atomic radicals will arrive at the reactor wall at which they may reflect, but will finally adsorb. There, new molecules can be generated which subsequently may desorb. In this way the dissociation in the plasma source is geometrically separated from the production zone of the molecules. Because the plasma production, plasma transport, and plasma-surface interactions are separated, the plasma conditions can be controlled independently from the downstream plasma chemistry, which allows independent studies of the different aspects of the process in a relatively simple manner.

We studied the formation of ammonia in expanding plasmas generated from: (a) expanding Ar plasma to which mixtures of N_2 and H_2 were added; (b) expanding H_2 plasma to which N_2 was added; (c) expanding N_2 plasma to which H_2 was added; (d) expanding $\text{N}_2\text{-H}_2$ plasma. By using various plasmas the relation between the NH_3 production and the fluxes of atomic N and H radicals, which increase from condition (a) to (d), can be studied. The density of NH_3 was measured with three different detection techniques, i.e., tunable diode laser absorption spectroscopy (TDLAS), cavity enhanced absorption (CEA) spectroscopy, and mass spectrometry. With mass spectrometry, also N_2 and H_2 can be detected, which is not possible with the two laser techniques.

FIG. 1. Schematic representation of the plasma source, vacuum vessel, and the plasma expansion with the recirculation flow in the chamber. The radius of the process chamber in all setups was 0.2 m, and the length of the plasma reactors was, respectively, 0.4 m (HNO), 0.6 m (Depo II), and 3 m (PLEXIS).

The laser techniques have the advantage that the measurements are not hampered by the presence of water as may be the case for ammonia using mass spectrometry. We investigated the efficiency and formation mechanism of ammonia generation in these plasmas under various plasma conditions and in three different plasma reactors, with different geometries.

We will first describe the basics of the ETP technique (Sec. II A). Next, in Sec. II B, the experimental details of the three techniques used to measure ammonia will be discussed, i.e., tunable diode laser absorption spectroscopy, cavity enhanced absorption spectroscopy, and mass spectrometry. In Sec. III, we will discuss the measured ammonia densities in the various plasmas. The conclusions are presented in the last section.

II. EXPERIMENTAL DETAILS

A. Expanding thermal plasma setup

To obtain high fluxes of reactive species, the expanding thermal plasma (ETP) technique was used. This technique, extensively described in literature (see, e.g., Ref. 23), is a remote technique in which reactive species are created in a high-pressure cascaded arc plasma source and the plasma processes take place downstream at lower pressure (Fig. 1). Here, only a short description of the main constituents is given.

In the cascaded arc plasma source a subatmospheric (typically 40 kPa) plasma is created with a power of 2–8 kW. The cascaded arc source consists of a 4 mm diameter bore channel of five water-cooled insulated copper plates with a total length of 30 mm. The cascaded plates are at floating potential. The last plate acts as the common anode for the discharge. A gas flow is admitted to the channel and a dc current is drawn from the three cathodes concentrically placed around the channel, to the grounded anode plate producing the plasma. The high heavy particle temperature of approximately 1 eV leads to almost full dissociation of molecular gases when these are injected in the arc. The plasma expands supersonically through a conically shaped nozzle into a low-pressure vessel (typically 20 Pa), and after a sta-

tionary shock, expands subsonically toward the other end of the process chamber. The position of the shock depends on the gases fed through the arc and is located 7 cm from the nozzle for an expanding Ar plasma and around 3 cm from the nozzle for an expanding N₂-H₂ plasma. As there is no power input anymore in the process chamber, the plasma is recombining. Furthermore, in the expansion, the electron temperature decreases to 0.1–0.3 eV. Dissociation and excitation by electrons can be neglected at these temperatures.²³

The resulting high-density plasma has an ionization degree of around 12% in argon²⁷ and around 1%–5% in pure nitrogen and mixtures of nitrogen and hydrogen.^{26,28} The current through the arc channel was set to 55 A in the experiments reported here and the voltage over the arc ranged from 40 V in argon plasmas to 150 V for N₂-H₂ plasmas. In the experiments, the pressure in the vessel was varied between 20 and 100 Pa by adjusting the gate valve to the pump.

N₂ and H₂ gas can also be injected into the background of the plasma vessel, i.e., into the recirculation flow in the chamber. If the source is operated on argon (or nitrogen), the injected molecules, together with molecules generated in the plasma vessel, form the basis of influx in the expanding plasma beam. It has been established that diffusion inwards occurs mainly in the subsonic region, but can also already occur in the supersonic region if the flow is rarefied.^{24,25} The point of inward diffusion is thus independent of the place where the gases are injected into the background. As a result, the gas mixture in the recirculation flow in the periphery of the chamber is mixed into the forward plasma beam emanating from the source. Molecules which diffuse into the expanding plasma beam can undergo charge-transfer with Ar⁺ (or N⁺) ions emanating from the source. Subsequent dissociative recombination reactions lead to atomic and/or molecular radicals. Furthermore, the monomers may undergo abstraction reactions with radicals, e.g., N atoms, leading to additional radicals.

Production of molecules out of atomic or molecular radicals in the volume by three-particle reactions can be excluded, since these reactions are too slow to lead to any significant production under our low-pressure conditions (mostly <100 Pa). This is certainly true for the time in the plasma beam, which is short (<1 ms). It holds also for the relatively long (0.1–1 s) residence time of particles, relevant for the background kinetics. However, during the residence time molecules may undergo reactions in the recirculation flow in the background of the plasma vessel, since even the lifetime of active particles as N and H atoms in the background is relatively long.

To determine the contribution of bimolecular nitrogen-hydrogen gas phase reactions to the ammonia generation, we modeled the chemistry in the expanding plasma beam and in the recirculation flow by a reaction model using the chemical kinetic software package CHEMKIN.²⁹ All possible reactions that can take place in N₂-H₂ plasma, with the rate constants as given in Ref. 30, are included in the model. From the results, we conclude that less than 1% of the measured ammonia density can be formed in the expanding plasma beam and that ammonia generation is not possible via gas phase reactions during the residence time in the vessel. Though we

cannot exclude the possibility that ammonia is formed at the end of the plasma source, when both nitrogen and hydrogen are fed through the plasma source, it is clear that also dissociation is very effective there. The results, which will be shown, indicate that no significant ammonia formation takes place at the end of the plasma source.

If the production of ammonia is due to plasma-surface interactions, a larger “active” surface to “active” volume ratio should lead to more ammonia production. The word “active” underlines the fact that the plasma(-surface) chemistry is dependent on geometry of the plasma reactors, i.e., the total surface or volume of the plasma reactor is not always used in the processes. The active surface to volume ratio is determined by the combination of the flow pattern of the plasma in the reactor and the total surface to volume ratio.

An indication that flow pattern and surface to volume ratio is important is offered by the use of three reactors of the same type (ETP-remote source), but different geometries. On the one hand there is a long (3 m), very effectively pumped reactor, PLEXIS, dedicated to these studies and in which most experiments were performed. On the other hand, two other similar reactors, HNO and Depo II (length, respectively, 0.4 and 0.6 m), which are much shorter with a larger active surface to volume ratio are used. The radius of the process chamber in all three setups was 0.2 m. All the experiments have been performed on clean stainless-steel walls. It is to be expected that in the last two reactors the surface generation is more effective than in the PLEXIS reactor in which the produced particles are more easily lost by pumping. This by itself already provides an indication of the significance of surface interactions for molecule generation.

The flow patterns in the vessel leading to the recirculation flows, depicted in Fig. 1, influence the plasma-surface interactions as they determine the effective area exposed to the fluxes of radicals and the time constants. Due to the recirculation flows, the complete wall of HNO and Depo II is exposed to a high flux of radicals. On the other hand, PLEXIS has an effective length of around 2 m, which is a factor of 5 larger than the HNO setup. In that case, not one recirculation pattern, but more recirculation patterns may exist along the axial direction in PLEXIS.³¹

It is evident that in PLEXIS, the loss of chemistry may be faster than in the relatively short Depo II and HNO experiments. Also, the surface/volume (S/V) ratio of the Depo II (14 m⁻¹) and HNO (16 m⁻¹) reactors is roughly a factor of 3 larger than that of PLEXIS (4 m⁻¹). We will later see that the efficiency of molecule production is correspondingly smaller in PLEXIS compared to the Depo II and HNO experiments.

In this respect also a difference in location of arrival of radicals may play a role. Hydrogen atoms diffuse more readily out of the plasma beam and arrive at surfaces closer to the source, whereas the heavier N atoms will arrive more at the downstream side. Also, this “mass-defocusing” effect may be more serious in the long PLEXIS reactor than in the other shorter reactors.

B. Diagnostics

1. Tunable diode laser absorption spectroscopy

In PLEXIS, we detected NH_3 in the downstream plasma by tunable diode laser absorption spectroscopy (TDLAS) at 70 cm from the plasma source. An infrared multicomponent acquisition (IRMA) system of the INP institute in Greifswald was used, which consists of four independent tunable diode lasers, which can be multiplexed.³² With this system, the mole fractions of several molecules can be simultaneously measured with millisecond time resolution. The laser beam from the IRMA system was directed twice through the vessel by the use of a retroreflector, to increase the path length and thus the sensitivity by a factor of 2.

The density of the produced NH_3 was monitored as function of various experimental parameters as the nitrogen and hydrogen flows, the background pressure in the plasma vessel, and the arc current. The density of ammonia was observed via the transition at 770.914 cm^{-1} with a line strength of $2.445 \times 10^{-20}\text{ cm}^{-1}/(\text{molecule cm}^{-2})$.³³

2. Cavity enhanced absorption spectroscopy

In PLEXIS, we also measured the density of NH_3 with cavity enhanced absorption (CEA) spectroscopy.³⁴ CEA spectroscopy with this setup has been performed previously to measure the ammonia generation in $\text{N}_2\text{-H}_2$ plasma,²² to study the ammonia spectrum in the $1.5\text{ }\mu\text{m}$ region,³⁵ and to demonstrate the feasibility of open-path trace gas detection of ammonia with CEA spectroscopy.³⁶

In the CEA measurements, the recorded ammonia spectra represented an average of 1000 scans, i.e., a measurement took about 30 s of acquisition time. After every measurement a spectrum was recorded without laser radiation coupled into the cavity to correct the ammonia spectra for the emission of the plasma. We note that the absorption spectrum over the full scanning range appears directly on the display of an oscilloscope in a fraction of a second. The recorded spectrum is a relative absorption spectrum expressed in loss of the empty cavity per round trip, i.e. $(1-R)/d$. The factor $(1-R)/d$ cannot directly be determined in the experimental configuration. The spectrum can be put on an absolute scale by measuring, e.g., the CEA spectrum of a known amount of a certain gas. We obtained the factor by recording the CEA spectrum of a known amount of water in the same frequency range as in which the ammonia transitions were measured. The H_2O transitions that were measured were the $6_{51} \leftarrow 5_{42}$ and the $6_{52} \leftarrow 5_{41}$ rotational transitions of the $(1, 1, 3) \leftarrow (0, 0, 0)$ vibrational band, and have line strengths of $1.13 \times 10^{-24}\text{ cm}^{-1}/(\text{molecule cm}^{-2})$ and $3.39 \times 10^{-24}\text{ cm}^{-1}/(\text{molecule cm}^{-2})$, respectively.³³ Using these line strengths and the known density of the ground-state water molecules of $2 \times 10^{23}\text{ m}^{-3}$, the factor $(1-R)/d$ was determined as $(5.5 \pm 0.5) \times 10^{-5}\text{ cm}^{-1}$. Since d was 1.1 m, a reflectivity of the mirrors of $R = 0.994 \pm 0.006$ was deduced from repeated measurements, which is in agreement with the manufacturer's specifications.

Ammonia was observed via the transitions in the combination band $\nu_1 + 2\nu_4$ reported by Lundsberg-Nielsen *et al.*³⁷ with the line positions 6568.299, 6568.401, and

FIG. 2. Mass scan as measured in expanding $\text{N}_2\text{-H}_2$ plasma (HNO setup). Both nitrogen and hydrogen were applied through the arc (0.8 slm N_2 and 1.2 slm H_2). The arc current was 55 A; the background pressure was kept constant at 20 Pa. NH_3 ($m/e=15, 16, 17$), N_2 ($m/e=14, 28, 29$), H_2 ($m/e=1, 2$), and H_2O ($m/e=16, 17, 18$) are detected.

6568.463 cm^{-1} , and absorption coefficients 7.556×10^{-4} , 7.602×10^{-4} , and $0.948 \times 10^{-4}\text{ cm}^{-1}\text{ Torr}^{-1}$. All CEA measurements have been performed at about 20 cm downstream from the exit of the arc. However, by moving the arc source it was verified that the NH_3 density was not dependent on the measurement position in the plasma.

3. Mass spectrometry

Depo II and HNO were equipped with a mass spectrometer for measurements of the stable species present in the background of the plasma. In the case of Depo II, a residual gas analyzer (Balzers Prisma 200 Quadrupole RGA) was attached with a pinhole to sample the gas in the reactor. HNO was equipped with a quadrupole mass spectrometer (Balzers QMS 421C) and the mass spectra were measured by sampling the gas through a controlled all-metal regulating valve (UDV 035). The operating pressure in the mass spectrometer unit was in the 10^{-5} – 10^{-4} Pa range depending on the chamber pressure. Absolute concentrations of the stable gas species N_2 , H_2 , and NH_3 were obtained by calibrating the mass spectrometer signals by injecting the relevant gases into the chamber at various known pressures.

In Fig. 2, a typical mass scan, after background subtraction, is shown as measured in an expanding $\text{N}_2\text{-H}_2$ plasma, with 0.8 slm (standard liter s^{-1}) N_2 and 1.2 slm H_2 flowing through the arc. The arc current was 55 A and the background pressure was 20 Pa. From the mass spectrometry measurements, we concluded that next to NH_3 ($m/e=15, 16, 17$), N_2 ($m/e=14, 28, 29$), H_2 ($m/e=1, 2$), and a small amount of H_2O ($m/e=16, 17, 18$), no other stable species were present in the plasma. In particular, no significant amounts of N_2H_4 or N_3H are found, confirming the generally observed dominance of NH_3 (and N_2 and H_2) generation. To show that this is valid for all relative hydrogen flow rates, the resulting molar fractions of N_2 , H_2 , and NH_3 and their sum are presented in Fig. 3, measured for a total flow of 1 slm (mass scan of Fig. 2 for 2 slm). The sum of the molar fractions turns out to be 0.985 ± 0.006 over the whole range of

FIG. 3. Relative amount of N_2 , H_2 , and NH_3 as measured by mass spectrometry as a function of the relative hydrogen flow rate in expanding N_2 - H_2 plasmas (HNO setup). Both nitrogen and hydrogen were applied through the arc at a total flow rate of 1 slm. The arc current was 55 A; the background pressure was kept constant at 20 Pa.

$0 \leq \phi_{H_2} / \phi_{total} \leq 1$ (with constant ϕ_{total}). The remaining 1.5% is the small amount of water always present in the plasma reactor.

III. RESULTS AND DISCUSSION

We studied the ammonia generation in four different expanding plasmas generated from mixtures of nitrogen and hydrogen as schematic depicted in Fig. 4: (a) expanding Ar plasma to which mixtures of N_2 and H_2 were added; (b) expanding H_2 plasma to which N_2 was added; (c) expanding N_2 plasma to which H_2 was added; (d) expanding N_2 - H_2 plasma. These plasma conditions were chosen to study the relation between the NH_3 production and the fluxes of atomic N and H radicals. In the conditions from (a) to (d), the amount of produced N and H atoms in the plasma increases and thus the flux of radicals toward the surface increases. In condition (a), the dissociation of N_2 and H_2 and thus the creation of N and H atoms can be controlled as the N and H radicals are produced in the plasma expansion by charge-transfer reactions. In conditions (b) and (c), the fluxes of, respectively, H and N atoms are optimized by applying the gas through the plasma source, while, respectively, N_2 and H_2 molecules are admixed downstream. In the final situation (d), both N_2 and H_2 are fed through the plasma source,

creating a plasma beam of mainly N and H atoms. In this way, the dependence of the ammonia production on the plasma composition and the role of N and H atomic radicals can be studied.

A. Expanding Ar plasma with N_2 and H_2 injected in the background

In the first experimental situation, an expanding argon plasma was created with 3 slm argon applied through the arc, and nitrogen and hydrogen were injected downstream into the background of the vessel. The characteristics of expanding Ar plasmas created with the cascaded arc source have been described extensively in literature²⁷ and here only the main issues will be discussed briefly. In the case of an expanding argon plasma, the plasma source emanates a partially ionized ($\sim 12\%$) argon flow. The metastable argon density Ar_m^* formed in three-particle recombination processes of the argon ions is typically a factor of 10 lower than the argon ion density³⁸ and we neglect the contribution of these states to the plasma chemistry. Molecules injected in the background mix with the recirculation flow, of which a part invades in the expanding plasma beam. These molecules are dissociated by charge-transfer reactions with argon ions from the plasma source followed by dissociative recombination leading to atomic N and H radicals,^{39–41}

In Fig. 5, the measured ammonia density as a function of the hydrogen flow rate relative to the total flow rate of nitrogen and hydrogen is depicted for three different conditions as measured by TDLAS on the PLEXIS setup. In conditions 1 and 2, an Ar flow of 3 slm was applied through the arc at an arc current of 55 A, and a total flow of nitrogen and hydrogen of 0.3 slm was injected in the background. The two conditions only differ in the value of the background pressure, i.e., 20 vs 100 Pa. At 55 A, the Ar flow is partially ionized (12%), i.e., an Ar^+ ion flow of 0.36 slm, as deter-

FIG. 4. Schematic representation of the expanding plasma jet for the four types of plasmas: (a) Ar plasma to which mixtures of N_2 and H_2 were added in the background; (b) H_2 plasma with N_2 injected into the background; (c) nitrogen plasma with H_2 injected in the background; (d) N_2 - H_2 plasma.

FIG. 5. Ammonia density in expanding Ar plasmas with N_2 and H_2 injected in the background. In conditions 1 and 2, the argon plasma was created with a flow of 3 slm Ar flowing through the arc. Simultaneously, a mixture of N_2 and H_2 molecules was admixed into the background of the vessel with a total flow rate of 0.3 slm. The arc current was set at 55 A; the background pressure was 20 Pa in condition 1 and 100 Pa in condition 2. In condition 3, the argon plasma was created with a flow of 5 slm Ar flowing through the arc, while $\phi_{N_2} + \phi_{H_2} = 0.5$ slm. The arc current was set at 75 A; the background pressure was 20 Pa.

mined from Langmuir probe measurements in the argon expansion,⁴² is injected into the vessel. Thus, the Ar^+ ion flow is approximately equal to the total injected flow of N_2 and H_2 molecules; thus, a significant dissociation of the molecules can be expected. In condition 3, an Ar flow of 5 slm was applied through the arc at an arc current of 75 A, and a total flow of nitrogen and hydrogen of 0.5 slm was injected in the background at a constant pressure of 20 Pa. In this case, the ionization degree is 15%, resulting in an Ar^+ ion flow of 0.65 slm, i.e., again the Ar^+ ion flow is approximately equal to the total injected flow of N_2 and H_2 molecules. The ammonia density in condition 3 is a factor of 1.8 higher compared to condition 1. Since more N_2 and H_2 molecules can be dissociated in condition 3 than in condition 1, this shows that the ammonia production is determined by the dissociation of the injected N_2 and H_2 .

The maximum in ammonia density is not observed at the stoichiometric ratio of H_2 and N_2 in NH_3 , but at lower fractions of H_2 . The reason for this is that Ar^+ ions are needed for the dissociation of both nitrogen and hydrogen molecules. Meulenbroeks *et al.*⁴⁰ have shown that the presence of small amounts of hydrogen in expanding plasmas leads to a strong decrease in the ionization degree of the plasma expansion. Also in this plasma, the charge-transfer reaction of Ar^+ with molecular hydrogen is 5 times faster than the reaction with molecular nitrogen [reaction (1) vs reaction (2)]. This means that less nitrogen is dissociated in the presence of hydrogen. The optimal N to H ratio leading to maximum NH_3 production is therefore already reached at lower hydrogen flows.

At 100 Pa (condition 2 in Fig. 5), the maximum ammonia production shifts to even lower hydrogen flows. At higher pressure, the charge-transfer reaction of Ar^+ with H_2 is faster than at 20 Pa, so now even at lower relative hydrogen flows, the ions are already almost completely consumed by hydrogen molecules. Thus, at higher relative hydrogen

FIG. 6. The use of N_2 and H_2 in the formation of NH_3 in condition 3 of Fig. 5 as a function of the relative hydrogen flow rate.

flows smaller amounts of atomic nitrogen are formed. The optimum ratio between N and H atoms at the surface to form ammonia is therefore already reached at even lower hydrogen flows.

As no other molecules than N_2 , H_2 , and NH_3 (besides Ar), are present in the plasma (Sec. II B 3), the use of N_2 and H_2 to form NH_3 can be calculated from Fig. 5. The use of N_2 (or H_2) is defined as the amount of N (or H) atoms in the formed NH_3 divided by the amount of N (or H) atoms admitted to the system in the form of N_2 (or H_2). The use of N_2 and H_2 gas in condition 3 is plotted in Fig. 6 as a function of the relative hydrogen flow. At small hydrogen flows, the fraction of the admitted H_2 , which is used for NH_3 formation, increases to 70%. On the other hand, the use of nitrogen at small nitrogen flows, thus high hydrogen flows, is never more than 15%. This discrepancy is explained by the fact that the dissociation of nitrogen decreases in the presence of hydrogen.

B. Expanding H_2 plasma with N_2 injected in the background

The plasma source was operated on 2 slm H_2 at an arc current of 55 A. The background pressure in the experiments was 20 Pa. Simultaneously, 0–1.5 slm N_2 was injected downstream. Under this experimental condition no ammonia was detected with the CEA technique in PLEXIS. From the detection limit of our CEA setup we conclude that less than 10^{18} m^{-3} ammonia is produced. The reason for this is that under this plasma condition only very few ions leave the source and thus N atoms can only be produced by the reaction³⁰

$$k = 2.7 \times 10^{-17} T^{0.5} \exp\left(\frac{-75\,900}{T}\right) \text{ m}^3 \text{ s}^{-1}. \quad (5)$$

However, this reaction is too endothermic to be effective. We conclude from these results that for the production of ammonia both H_2 and N_2 need to be dissociated and thus H atoms and N atoms are essential.

C. Expanding N₂ plasma with H₂ injected in the background

In PLEXIS, the ammonia generation in expanding argon plasmas to which nitrogen and hydrogen were admixed was hampered by the amount of N radicals produced in the plasma (Sec. III A). To increase the amount of N radicals, an expanding nitrogen plasma is generated and hydrogen is added downstream into the plasma. In a pure nitrogen plasma, the dissociation degree of N₂ in the arc is expected to be up to 35%, while an ionization degree of around 1%–5% is reached.^{26,28} The densities of the metastable N atoms, N(²P) and N(²D), emanating from the plasma source are expected to be at maximum in the order of 20% of the N(⁴S) atoms (assuming a thermal population at a temperature of 1 eV). In the expansion, the N(²P) and N(²D) densities decrease due to deexcitation by collisions with electrons, N(⁴S) atoms, N₂ molecules, or the nozzle wall. Deexcitation will also limit the densities of metastable N atoms produced in the expansion by dissociative recombination of N₂⁺ with electrons. Note that the production via N₂⁺ would be directly linked to the ion density, i.e., to the ionization degree of the plasma.

All experiments until now have been performed with a long nozzle installed in the plasma source. However, Vankan *et al.*⁴³ proved that the main loss channel for radicals produced in the plasma source is surface recombination on the nozzle surface. They showed that in pure expanding H₂ plasmas the use of a short nozzle results in a 10 times higher atomic H flux. By shortening the length of the nozzle, the surface area is reduced and thus the atomic flux is increased. Although we did not measure the atomic N flux in pure nitrogen plasmas produced using the short nozzle, we expected that this loss mechanism is similarly important for the nitrogen atoms. We therefore measured the ammonia density in PLEXIS with a long (length of $L=14$ mm) and a short nozzle ($L=7$ mm).

The ammonia density as measured in PLEXIS is plotted in Fig. 7(a) as a function of the hydrogen flow rate relative to the total flow rate. The ammonia densities in PLEXIS with a long and a short nozzle were measured by CEA spectroscopy and TDLAS, respectively. In the experiments, the plasma source was operated on 2 slm N₂ at an arc current of 55 A. Simultaneously, hydrogen molecules were admixed into the background of the vessel with a flow rate of 0–1.5 slm. The downstream pressure was kept constant at 100 Pa.

With the long nozzle installed, the ammonia density increased with increasing hydrogen flow and saturated at a level of $2.5 \times 10^{19} \text{ m}^{-3}$ for relative hydrogen flows larger than 0.26 [Fig. 7(a)]. This means that at $T=600$ K, which is determined from the Doppler width of the measured ammonia transitions, 0.2% of the background gas is ammonia. The saturation of the ammonia density can be explained by noting that the hydrogen molecules, which are injected in the background, can only be dissociated by N atoms and N⁺ ions, which are however less present than N atoms, emanating from the arc. We determined that mainly N atoms are responsible for the dissociation of H₂, resulting in NH radicals,

FIG. 7. Ammonia density in expanding N₂ plasmas with H₂ injected in the background. (a) The nitrogen plasma was created with a flow of 2 slm in PLEXIS flowing through the arc. Simultaneously, hydrogen molecules were admixed into the background of the vessel with a flow rate of 0–1.5 slm. The arc current was set at 55 A; the background pressure was 100 Pa. (b) The nitrogen plasma in Depo II was created with 1 slm N₂ while the other conditions were the same. The background pressure was 20 Pa.

which has a rate constant of $4 \times 10^{-16} \text{ m}^3 \text{ s}^{-1}$ in our plasmas. In a later article, it will be shown that NH in a follow-up reaction with N and H atoms is dissociated, resulting in mainly N and H atoms. Next to this process, hydrogen molecules can also efficiently be dissociated by charge-transfer reactions with N⁺ followed by dissociative recombination as proposed by Vankan *et al.*,²²

with reaction rates of, respectively, $k=5.4 \times 10^{-16} \text{ m}^3 \text{ s}^{-1}$ and $k \approx 10^{-13} \text{ m}^3 \text{ s}^{-1}$,³⁰ producing two H atoms and one N atom, all of which can be used for the production of ammonia. The production of H containing radicals (H, NH) will increase until all N atoms and N⁺ ions are consumed, limited by the time these reactions can take place. This also explains the saturation, as adding more H₂ molecules does not lead to the production of more H atoms, and thus no extra NH₃ is produced.

The NH₃ density increased by a factor of 5 using a short nozzle [Fig. 7(a)]. This must be ascribed to a higher dissociation degree of the nitrogen plasma ejected from the source. This conclusion must be drawn, despite the fact that

FIG. 8. The use of N_2 and H_2 in the formation of NH_3 in Depo II [Fig. 7(b)] as a function of the relative hydrogen flow rate.

the reported values of loss probability of H and N atoms on copper differ appreciably. The loss probability of H atoms and N atoms on copper surfaces is reported to be 0.3 to 0.5 (Refs. 44 and 45) and 3.9×10^{-2} to 8.5×10^{-4} ,^{46,47} respectively.

In Depo II, the ammonia density was measured with mass spectrometry. The plasma source with a long nozzle installed was operated on 1 slm N_2 at an arc current of 55 A and the downstream pressure was kept constant at 20 Pa. The ammonia density saturated at a level of $3 \times 10^{19} \text{ m}^{-3}$ for relative hydrogen flows larger than 0.13 [Fig. 7(b)]. This means that 0.6% of the background gas was ammonia. The ammonia density in PLEXIS saturated at twice the relative hydrogen flow, because the initial nitrogen flow is also twice as large, leading to twice as much N atoms and N^+ ions.

Again, the use of N_2 and H_2 to form NH_3 can be calculated. The use of H_2 and N_2 gas in Depo II is plotted in Fig. 8 as a function of the relative hydrogen flow. At small hydrogen flows, the fraction of the admitted H_2 which is used for NH_3 formation is 20% and decreases with higher hydrogen flows. The decrease is due to the fact that at a certain relative hydrogen flow rate adding more H_2 molecules does not lead to the production of more NH_3 molecules as explained before. On the other hand, the use of nitrogen is always 2% or less. The low use of N_2 gas indicates that the ammonia production is limited by the amount of H radicals produced.

At the condition of 0.45 slm H_2 injected in the background, the ammonia density was measured as a function of the background pressure in PLEXIS from 10 to 200 Pa as shown in Fig. 9. The measured ammonia density shows a linear dependence on pressure. This can be explained assuming that only N and H atomic radicals are involved in the production of ammonia. The H atoms are mainly produced by the reaction between N atoms and H_2 molecules [reaction (6)], and dissociation of the resulting NH radicals with N atoms. The atomic N flow is only dependent on the cascaded arc source parameters and remains thus constant, when the pressure in the vessel is changed. This means that the amount of H produced in the experiments is independent of pressure. The total amount of NH_3 formed is then also constant, but its

FIG. 9. Ammonia density as a function of the background pressure in the vessel as measured with CEA spectroscopy. The plasma is created with 2 slm N_2 flowing through the arc at an arc current of 55 A and 0.45 slm H_2 injected in the background.

residence time τ in the vessel increases with increasing pressure, i.e., $n_{NH_3} \propto \tau$. And, since τ is linearly dependent on the pressure in the vessel, the ammonia density should also increase linearly with increasing pressure. Furthermore, this indicates that three-particle reactions are not responsible for the ammonia production, because the ammonia density would then show a stronger than linear dependence on the pressure, which is not observed. Moreover, under all conditions the density of ammonia proved to be independent of the axial and lateral position in the plasma jet at which the CEA spectrum was taken. This shows that ammonia is not produced in the expanding plasma jet. All these observations together with the results from the CHEMKIN simulations discussed in Sec. II A are consistent with wall production of ammonia.

D. Expanding N_2 - H_2 plasma

In the previous section (Sec. III C), the ammonia generation was limited by the amount of H radicals produced in the plasma by the dissociation of H_2 by N atoms and N^+ ions, but much less, from the source. To optimize the dissociation of both nitrogen and hydrogen, the plasma in the fourth experimental situation was produced with both nitrogen and hydrogen fed through the plasma source. The experiments were performed on all three plasma reactors, which all had clean stainless-steel walls. In HNO and PLEXIS the total flow was 2 slm, and in Depo II the total flow was 1 slm. The current through the arc was set at 55 A and the downstream pressure was kept constant at 20 Pa. In the experiments, the hydrogen flow rate relative to the constant total flow rate was varied. The plasma contains mainly nitrogen and hydrogen atoms and molecules, since most of the ions (N^+ , H^+) are lost very fast—most probably even faster than in the previous case as now H_2 is already present in the source—via charge-transfer reactions with hydrogen molecules in the beginning of the expansion.

In Fig. 10, the ammonia molar fractions as a function of the hydrogen flow rate relative to the total flow rate, as was measured in N_2 - H_2 plasmas in the three setups, are plotted. In the case of HNO and Depo II, the ammonia density was

FIG. 10. Relative amount of ammonia as a function of the relative hydrogen flow rate in expanding N_2 - H_2 plasmas. Both nitrogen and hydrogen were applied through the arc, in PLEXIS and HNO at a total flow rate of 2 slm and in Depo II at a total flow rate of 1 slm. The arc current was 55 A; the background pressure was kept constant at 20 Pa.

measured with mass spectrometry. The ammonia densities in PLEXIS in the experiments with the long and short nozzles were measured by CEA spectroscopy and TDLAS, respectively. The maximum ammonia molar fraction increased from 2% in PLEXIS to about 10% in Depo II and HNO. The normalized NH_3 molar fractions are plotted in Fig. 11, which shows that the trend of ammonia as a function of the hydrogen flow rate relative to the total flow rate is the same in all setups. Only the absolute amounts differ: the production is the largest in HNO and Depo II, the two smaller volume reactors and the smallest in PLEXIS, with the large volume. This is in agreement with the remarks made in Sec. II A that we expect that the ammonia density is dependent on the “active” surface to volume ratio and should be the highest in HNO and Depo II, and the lowest in PLEXIS. This is in line with the idea that ammonia is generated at the wall.

As under the conditions discussed in Sec. III A, N_2 and H_2 injected in an Ar plasma expansion, also in the case of N_2 and H_2 flowing through the arc, the maximum ammonia production is not observed at the stoichiometric ratio of hydrogen and nitrogen in ammonia. This is *a priori* not to be expected, since the dissociation degree of the plasma source

FIG. 11. Normalized ammonia molar fraction as a function of the relative hydrogen flow rate in expanding N_2 - H_2 plasmas. The curve is reproduced from Fig. 6 of Ref. 16 and presents a self-consistent model in which it is assumed that NH_3 is mainly produced at the surface of the vessel in a low-pressure (2 Torr) flowing discharge.

for different flow ratios of N_2 and H_2 could change greatly. For expanding N_2 - H_2 plasma the ammonia density increased by a factor of 2 in PLEXIS, when the long nozzle was replaced by a short nozzle. The same reasoning as mentioned in Sec. III C is also applicable to expanding N_2 - H_2 plasmas for the N and H fluxes. An increase of N and H flux, due to less loss in the nozzle, leads to an increase in ammonia generation. Furthermore, this shows that the ammonia in the plasma chamber does not originate from plasma-surface interactions at the nozzle wall, but from the surface in the vessel, because with a shorter nozzle a decrease in the NH_3 generation would have been observed.

The trend of the ammonia molar fraction as a function of the hydrogen flow rate relative to the total flow rate, as shown in Fig. 10, is generally observed in N_2 - H_2 plasmas (rf, microwave, barrier discharge, low-pressure dc flowing discharge).^{9,21,48} The resulting curve of a self-consistent model of the ammonia production in a low-pressure (270 Pa) flowing discharge as presented by Gordiets *et al.*¹⁶ is also depicted in Fig. 11.

In the model it is assumed that NH_3 is mainly produced at the surface of the vessel by the stepwise addition reactions between adsorbed nitrogen and hydrogen containing radicals at the surface and incoming atomic N and H radicals.¹⁶ Their proposed reaction mechanism at the surface was validated by others^{17,18} and can be summarized as follows:

From the strong similarity of the self-consistent model with our measurements, we conclude that in the present experiments ammonia is formed at the surface via the above reaction mechanism.

1. Influence of surface material on ammonia production

To investigate the influence of the wall material of the plasma reactor on the ammonia production in expanding N_2 - H_2 plasma, we measured the ammonia density in a clean stainless-steel vessel and with a 1 μm a -SiN_x layer deposited on the reactor wall in Depo II. The ammonia molar fraction as deduced from mass spectrometry measurements as a function of the relative hydrogen flow rate proves to be the same for both wall materials (Fig. 12). This indicates that the ammonia production is independent of the wall material. This seems to be in contrast to experiments of various research groups in the world, in which it was shown that the ammonia production is dependent on the type of wall material, e.g., iron, stainless-steel, copper, nickel, silver, aluminum, Pyrex, zinc, or platinum.^{9–13} However, a major difference with our experiments is that in those experiments the wall is used to form adsorbed nitrogen atoms by the dissociative adsorption

FIG. 12. Ammonia molar fraction as a function of the relative hydrogen flow rate as measured by mass spectrometry in Depo II in expanding N_2 - H_2 plasmas with and without α - SiN_x deposited on the reactor wall. Both nitrogen and hydrogen were applied through the arc at a total flow rate of 1 slm. The arc current was 55 A; the background pressure was kept constant at 20 Pa.

of excited N_2 molecules or nitrogen molecular ions. The adsorbed nitrogen atoms react with impinging hydrogen atoms or molecules from the plasma. In our experiments, the N and H radicals are already produced in the plasma and as a result the fluxes of N and H radicals to the surface are around $10^{21} \text{ m}^{-2} \text{ s}^{-1}$,²⁴ which is one order of magnitude higher than in the other experiments.

We observed that the ammonia molar fraction is independent of the two wall materials studied, which indicates that the N and H flux to the surface is most likely not changed by an α - SiN_x deposited wall. The high N and H flux to the surface leads to a surface covered with N and H radicals and other molecular radicals. This coverage passivates the surface, i.e., the actual wall material is screened off and the surface processes become more or less independent of the actual wall material. The actual chemistry takes place in an additional layer at the passivated surface. The presence of weakly bonded radicals at a surface was previously suggested by Gordiets *et al.*⁴⁹ to explain the NO production in N_2 - O_2 plasmas, by Gelb *et al.*⁵⁰ to explain atomic recombination on surfaces, and was observed in ammonia decomposition experiments on ruthenium.⁵¹

2. Pressure decrease

In the experiments discussed up until now, the pressure was kept constant while the hydrogen flow rate relative to the total flow rate was changed. In experiments with a constant flow through the plasma source, constant pumping speed, assuming a constant temperature, and no change in the amount of particles in the vessel, one expects a constant pressure in the vessel and constant residence times for the particles. Consider now the production of ammonia from nitrogen and hydrogen by the reaction: $N_2 + 3H_2 \rightarrow 2NH_3$. This means that if two molecules of NH_3 are formed from one N_2 molecule and three H_2 molecules, the total number of molecules decreases by two. Since the pressure in the vessel is linearly dependent on the number of molecules, we should observe a pressure decrease in the vessel with the same trend as in Fig. 10. With a starting background pressure of 22 Pa

FIG. 13. Relative decrease of the pressure in the vessel as a function of the relative hydrogen flow rate as measured in expanding N_2 - H_2 in HNO. Both gases were applied through the arc with a total flow of 2 slm at an arc current of 55 A. The starting background pressure was 22 Pa for a pure nitrogen plasma.

for a pure nitrogen plasma, a relative pressure decrease was found with a maximum of 11% in HNO for expanding N_2 - H_2 as shown in Fig. 13. The observed pressure change occurred only when the plasma source was operated on a mixture of N_2 and H_2 ; the pressure was observed to remain constant at 22 Pa for the pure hydrogen and nitrogen plasmas. This decrease is not due to the pumping system, as the pumping capacity is constant and independent of the gas type. Second, it is not caused by a temperature change, because the pressure is observed to change almost instantaneously after adjustment of the flows. Therefore, we concluded that more than 10% of the total background pressure is ammonia, as was also concluded from the NH_3 measurements in HNO plotted in Fig. 10.

3. Efficiency of the ammonia generation

As no other molecules besides N_2 , H_2 , and NH_3 are present in the plasma (Sec. II B 3), the use of N_2 and H_2 must be equivalent to the amount of gas needed to produce NH_3 . The use of N_2 and H_2 gases as determined from mass spectrometry measurements in HNO is plotted in Fig. 14.

FIG. 14. The use of N_2 and H_2 for NH_3 production as a function of the relative hydrogen flow rate as measured in expanding N_2 - H_2 plasmas by mass spectrometry. Both gases were applied through the arc with a total flow of 2 slm at an arc current of 55 A; the background pressure was kept constant at 20 Pa.

The results at low flows of N_2 and H_2 indicate that the minority gas is almost fully dissociated, i.e., a dissociation degree of at least 60% for H_2 gas for small H_2 flows and 48% for N_2 gas for small N_2 flows. This means that about 10^{20} atomic N and H radicals per second arrive at the reactor wall at which they will react with particles at the surface.

The use of H_2 and N_2 can be made plausible in a picture that at the passivated (stainless-steel) surface only H atoms, N atoms and NH_x ($x=1,2$) radicals can be present. At small hydrogen fractions the surface will then only be covered with N and NH_x radicals. Incoming N radicals form N_2 molecules by association with N atoms on the surface or adsorb at surface sites. The few H atoms impinging at the surface will readily form NH_x radicals and finally NH_3 molecules which desorb. With increasing hydrogen flow, the H coverage on the surface increases. Then, the H atoms impinging at the surface are more and more converted back into H_2 molecules, or adsorb at surface sites, or are used to form NH_x radicals. The N-atom flux toward the surface decreases with increasing hydrogen flow. As a result, the N atoms impinging on the surface react mainly with H atoms on the surface leading to NH radicals on the surface. These are quickly hydrogenated by the incoming H-atom flux. This results in an increasing use of N_2 . The above picture is in agreement with the general proposed reaction mechanism for the ammonia production at the surface in N_2 - H_2 plasmas,^{16–18} but also in surface studies related to catalysis.^{6,7,52–54} In conclusion, ammonia is mainly produced by association of atomic and molecular radicals at the surface, e.g., by the successive hydrogenation of adsorbed nitrogen atoms and the intermediates NH and NH_2 at the surface of the plasma reactor.

That 11% of the background gas is ammonia (Figs. 10 and 13) is a remarkable result if one compares this with the total ammonia that could have been produced in our experimental conditions. To estimate the efficiency of the ammonia generation in our experiments, let us assume that a dissociation degree of 60% for H_2 and 48% for N_2 gas is applicable over the whole range of the hydrogen flow rate relative to the total flow rate of nitrogen and hydrogen. Furthermore, we assume that all H and N atoms are used to produce ammonia, i.e., 3 H atoms per 1 N atom, only limited by the availability of one of the atomic radicals. The maximum ammonia molar fraction that could have been generated in the experiments would have been 30% at a relative hydrogen ratio of 0.7. This means that an efficiency in the ammonia generation of 33% is achieved in our experiments.

IV. CONCLUSIONS

We studied the ammonia generation in four different types of expanding plasmas containing mixtures of nitrogen and hydrogen. In the experiments, the plasma is used to dissociate the precursor molecules already before they come in contact with a surface, and the surface is then exposed to large fluxes of atomic and molecular radicals. The efficiency and formation mechanisms of ammonia generation were determined under various plasma conditions and in three similar plasma reactors, with different geometries. Three diagnostic techniques, i.e., tunable diode laser absorption

spectroscopy, cavity enhanced absorption spectroscopy, and mass spectrometry, were employed to measure the ammonia density.

We have shown that the ammonia production is strongly dependent on the fluxes of atomic N and H radicals to the surface. To produce large amounts of ammonia, nitrogen gas has to be dissociated in the plasma source and not injected in the background. By using an atomic nitrogen and hydrogen source, ammonia can be formed efficiently, i.e., more than 10% of the total background pressure is measured to be ammonia. The ammonia density was the highest in the plasma reactor with the highest “active” surface to volume ratio. This is in line with the picture that ammonia is generated at the surface exposed to plasma. Furthermore, our results indicate that the ammonia production is independent of wall material, contrary to other experiments in which a material dependence was observed. The explanation is that the fluxes of N and H radicals in our experiments are two orders of magnitude higher. This results in a passivated surface, covered with N, H and NH and NH_2 radicals. The actual chemistry leading to the formation of ammonia at the surface takes place in an additional layer on top of the passivated surface. Our results for expanding N_2 - H_2 plasma are in agreement with reported trends in literature, which were explained by the production of ammonia at the surface through plasma-surface interactions. We therefore conclude that ammonia is formed via plasma-surface interactions by stepwise addition reactions between adsorbed nitrogen and hydrogen containing radicals at the surface and incoming atomic H radicals, e.g., by the successive hydrogenation of adsorbed nitrogen atoms and the intermediates NH and NH_2 at the surface of the plasma reactor.

ACKNOWLEDGMENTS

We acknowledge P. Vankan and T. Rutten for their contribution during the measurements and M.J.F. van de Sande, J.F.C. Jansen, A.B.M. Hüsken, and H.M.M. de Jong for the technical assistance. This work is part of the research program of the Foundation for Fundamental Research on Matter (FOM), which is financially supported by the Netherlands Organization for Scientific Research (NWO). The authors would like to thank the Center for Plasma Physics and Radiation Technology (CPS) for financially supporting the collaboration between the Eindhoven University of Technology (TU/e) and the Institut für Niedertemperatur-Plasmaphysik (INP).

¹K. Tamaru, in *Catalytic Ammonia Synthesis*, edited by J. Jennings (Plenum, New York, 1991), p. 1.

²V. Smil, *Nature* (London) **400**, 415 (1999).

³M. D. Fryzuk, *Nature* (London) **427**, 498 (2004).

⁴S. R. Tennison, in *Catalytic Ammonia Synthesis*, edited by J. Jennings (Plenum, New York, 1991), p. 303.

⁵K. Aika, *Angew. Chem., Int. Ed. Engl.* **25**, 558 (1986).

⁶G. Ertl, in *Catalytic Ammonia Synthesis*, edited by J. Jennings (Plenum, New York, 1991), p. 109.

⁷C. Zhang, Z.-P. Liu, and P. Hu, *J. Chem. Phys.* **115**, 609 (2001).

⁸O. Nomura, H. Oyama, and Y. Sakamoto, *Sci. Pap. Inst. Phys. Chem. Res. (Jpn.)* **75**, 124 (1981).

⁹E. N. Eremin, A. N. Mal'tsev, and V. M. Belova, *Russ. J. Phys. Chem.* **45**, 635 (1971).

¹⁰M. Tanaka, H. Uyama, and O. Matsumoto, *Plasma Chem. Plasma Process.*

- 14**, 491 (1994).
- ¹¹K. S. Yin and M. Venugopalan, *Plasma Chem. Plasma Process.* **3**, 343 (1983).
- ¹²H. Kiyooka and O. Matsumoto, *Plasma Chem. Plasma Process.* **16**, 547 (1996).
- ¹³M. Touvelle, J. L. M. Licea, and M. Venugopalan, *Plasma Chem. Plasma Process.* **7**, 101 (1987).
- ¹⁴H. Uyama and O. Matsumoto, *Plasma Chem. Plasma Process.* **9**, 13 (1989).
- ¹⁵B. Gordiets, C. M. Ferreira, M. J. Pinheiro, and A. Ricard, *Plasma Sources Sci. Technol.* **7**, 363 (1998).
- ¹⁶B. Gordiets, C. M. Ferreira, M. J. Pinheiro, and A. Ricard, *Plasma Sources Sci. Technol.* **7**, 379 (1998).
- ¹⁷A. Ricard, B. F. Gordiets, M. J. Pinheiro, C. M. Ferreira, G. Baravian, J. Amorim, S. Bockel, and H. Michel, *Eur. Phys. J.: Appl. Phys.* **4**, 87 (1998).
- ¹⁸J. L. Jauberteau, I. Jauberteau, and J. Aubreton, *J. Phys. D* **35**, 665 (2002).
- ¹⁹W. M. M. Kessels, F. J. H. van Assche, J. Hong, D. C. Schram, and M. C. M. van de Sanden, *J. Vac. Sci. Technol. A* **22**, 96 (2004).
- ²⁰H. Kim, *J. Vac. Sci. Technol. B* **21**, 2231 (2003).
- ²¹H. Nagai, M. Hiramatsu, M. Hori, and T. Goto, *J. Appl. Phys.* **94**, 1362 (2003).
- ²²P. Vankan, T. Rutten, S. Mazouffre, D. C. Schram, and R. Engeln, *Appl. Phys. Lett.* **81**, 418 (2002).
- ²³M. C. M. van de Sanden, R. J. Severens, W. M. M. Kessels, R. F. G. Meulenbroeks, and D. C. Schram, *J. Appl. Phys.* **84**, 2426 (1998); **85**, 1243(E) (1999).
- ²⁴P. Vankan, S. Mazouffre, R. Engeln, and D. C. Schram, *Phys. Plasmas* **12**, 102303 (2005).
- ²⁵R. Engeln, S. Mazouffre, P. Vankan, D. C. Schram, and N. Sadeghi, *Plasma Sources Sci. Technol.* **10**, 595 (2001).
- ²⁶S. Mazouffre, I. Bakker, P. Vankan, R. Engeln, and D. C. Schram, *Plasma Sources Sci. Technol.* **11**, 439 (2002).
- ²⁷M. C. M. van de Sanden, J. M. de Regt, G. M. Jansen, J. A. M. van der Mullen, D. C. Schram, and B. van der Sijde, *Rev. Sci. Instrum.* **63**, 3369 (1992).
- ²⁸R. P. Dahiya, M. J. de Graaf, R. J. Severens, H. Swelsen, M. C. M. van de Sanden, and D. C. Schram, *Phys. Plasmas* **1**, 2086 (1994).
- ²⁹CHEMKIN interface 4, distributed by Reaction Design (available online at www.ReactionDesign.com).
- ³⁰M. Capitelli, C. M. Ferreira, B. F. Gordiets, and A. I. Osipov, *Plasma Kinetics in Atmospheric Gases* (Springer, Berlin, 2000).
- ³¹H. van Eck (private communication).
- ³²J. Röpcke, L. Mechold, M. Kanning, J. Anders, F. G. Wienhold, D. Nelson, and M. Zahniser, *Rev. Sci. Instrum.* **71**, 3706 (2000).
- ³³L. S. Rothman, A. Barbe, D. C. Benner, L. R. Brown, C. Camy-Peyret, M. R. Carleer, K. Chance, C. Clerbaux, V. Dana, V. M. Devi *et al.*, *J. Quant. Spectrosc. Radiat. Transf.* **82**, 5 (2003).
- ³⁴R. Engeln, G. Berden, R. Peeters, and G. Meijer, *Rev. Sci. Instrum.* **69**, 3763 (1998).
- ³⁵G. Berden, R. Peeters, and G. Meijer, *Chem. Phys. Lett.* **307**, 131 (1999).
- ³⁶R. Peeters, G. Berden, A. Apituley, and G. Meijer, *Appl. Phys. B: Lasers Opt.* **71**, 231 (2000).
- ³⁷L. Lundsberg-Nielsen, F. Hegelund, and F. M. Nicolaisen, *J. Mol. Spectrosc.* **162**, 230 (1993).
- ³⁸A. J. M. Buuron, D. K. Otorbaev, M. C. M. van de Sanden, and D. C. Schram, *Phys. Rev. E* **50**, 1383 (1994).
- ³⁹G. J. H. Brussaard, Ph.D. thesis, Eindhoven University of Technology, Eindhoven (1999); available online at <http://alexandria.tue.nl/extra2/9900312.pdf>.
- ⁴⁰R. F. G. Meulenbroeks, A. J. van Beek, A. J. G. van Helvoort, M. C. M. van de Sanden, and D. C. Schram, *Phys. Rev. E* **49**, 4397 (1994).
- ⁴¹J. Peterson, A. L. Padellec, H. Danared, G. Dunn, M. Larsson, A. Larson, R. Peverall, C. Strömholm, S. Rosén, M. af Ugglas *et al.*, *J. Chem. Phys.* **108**, 1978 (1998).
- ⁴²M. A. Blauw, Internal Report, Eindhoven University of Technology (2004).
- ⁴³P. Vankan, R. Engeln, and D. C. Schram, *Appl. Phys. Lett.* **86**, 101501 (2005).
- ⁴⁴B. Jackson and M. Pearson, *J. Chem. Phys.* **96**, 2378 (1992).
- ⁴⁵C. T. Rettner, *Phys. Rev. Lett.* **69**, 383 (1992).
- ⁴⁶G. G. Mannella, *Chem. Rev. (Washington, D.C.)* **63**, 1 (1963).
- ⁴⁷J.-P. Sarrette, B. Rouffet, and A. Ricard, *Plasma Processes Polym.* **3**, 120 (2006).
- ⁴⁸J. Amorim, G. Baravian, and G. Sultan, *Appl. Phys. Lett.* **68**, 1915 (1996).
- ⁴⁹B. Gordiets, C. M. Ferreira, J. Nahorny, D. Pagnon, M. Touzeau, and M. Vialle, *J. Phys. D* **29**, 1021 (1996).
- ⁵⁰A. Gelb and S. K. Kim, *J. Chem. Phys.* **55**, 4935 (1971).
- ⁵¹C. J. Hagedorn, M. J. Weiss, and W. H. Weinberg, *J. Vac. Sci. Technol. A* **16**, 984 (1998).
- ⁵²Z.-P. Liu, P. Hu, and M.-H. Lee, *J. Chem. Phys.* **119**, 6282 (2003).
- ⁵³H. Shi, K. Jacobi, and G. Ertl, *J. Chem. Phys.* **102**, 1432 (1995).
- ⁵⁴R. M. van Hardeveld, R. A. van Santen, and J. W. Niemantsverdriet, *J. Vac. Sci. Technol. A* **15**, 1558 (1997).