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Characterization of the high-voltage pulsed discharge plasma of ammonia by emission spectroscopy*

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We have used optical emission spectroscopy to characterize the high-voltage pulsed discharge of ammonia. Ammonia was highly dissociated in the discharge at low pressures. More atomic nitrogen was generated as compared to the discharge of nitrogen gas at the same pressure of 0.8kPa. We discuss the elimination of the oxygen impurity in the ammonia discharge, and we estimate the time-dependent atomic excitation temperature and the electron density from the measured spectra.

Keywords: photoemission spectroscopy, plasma, electric discharge
PACC: 5200, 7960

1. Introduction

The synthesis of various types of nitride has attracted increasing attention because of their novel properties and wide applications. For instance, the III nitrides have been applied as optical devices in the blue and ultraviolet regions as well as high-temperature devices.[1,2] Research on carbon nitride materials has been triggered to a large extent by the theoretical prediction that the hardness and thermal conductivity of β-C_3N_4 are near those of diamond.[3]

Since atomic nitrogen plays an important role in the synthesis of nitrides due to its high chemical reactivity, the concentration of atomic nitrogen in the nitrogen source is of significant concern. Nitrogen gas is often used as the working gas in the discharge, such as radio frequency (rf), microwave, arc or hollow cathode discharges[4−7] etc. The discharge can generate a temperature of several eV or even tens of eV to dissociate nitrogen molecules effectively, which cannot be reached by conventional heating. The method of high-voltage dc pulsed discharge can be applied in a wider range of gas pressures. The set-up for discharge is rather simple and inexpensive because the average power is low, and the dissociation undergoes more efficiently due to its higher discharge current as compared with other kinds of discharge as mentioned above. Hence, pulsed discharge is a good choice when combined with pulsed laser ablation.

In our previous work with pulsed discharges of nitrogen and laser ablation of metal aluminium,[8] a very high concentration of atomic nitrogen species was produced and high-purity AlN powders were synthesized under higher gas pressures (>5kPa). However, under lower gas pressures (<2kPa), the nitrogen molecules could not be dissociated effectively. In the synthesis of nanosized particles by laser ablation, the size of the produced particles is significantly dependent on the environment pressure.[9] In attempting to obtain a high concentration of atomic nitrogen under a lower environment pressure, ammonia is expected to be a good candidate because its dissociation and ionization energies are much lower than those of nitrogen molecules. As a nitrogen source, ammonia has been successfully used to synthesize nitrides, such as β-C_3N_4 and AlN.[10−12]

In this present work, the pulsed discharge plasma of ammonia at a low pressure of 0.8kPa was characterized by emission spectroscopy and compared with the discharge of nitrogen gas. The transient excitation temperatures of H atoms and N ions in the discharge plasma were estimated by the Boltzmann plot method. The electron density in the plasma was calculated from the Stark broadening of the hydrogen H

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β line at 486.1 nm. We discuss th elimination of the oxygen impurity in the discharge of ammonia.

2. Experimental details

The pulsed discharge circuit was very simple, as shown in Fig.1. It was a design often used for pulsed gas lasers in earlier years. In brief, a spark gap (SG) was used to switch the pulsed discharge circuit. The externally triggered discharge of the spark gap led to the discharge between the electrodes in the chamber. The discharge voltage and pressure could therefore be adjusted over a wide range. Compared with rf or microwave discharges, this device can generate much higher discharge currents. A typical high voltage used in our experiments was 5.0kV. Since the pulsed discharge was run only at a repetition rate of 10Hz, a small power supply was adequate as the average current was low. A pair of tungsten electrodes was set in a vacuum chamber and the distance between them can be adjusted according to the discharge voltage and the gas pressure.

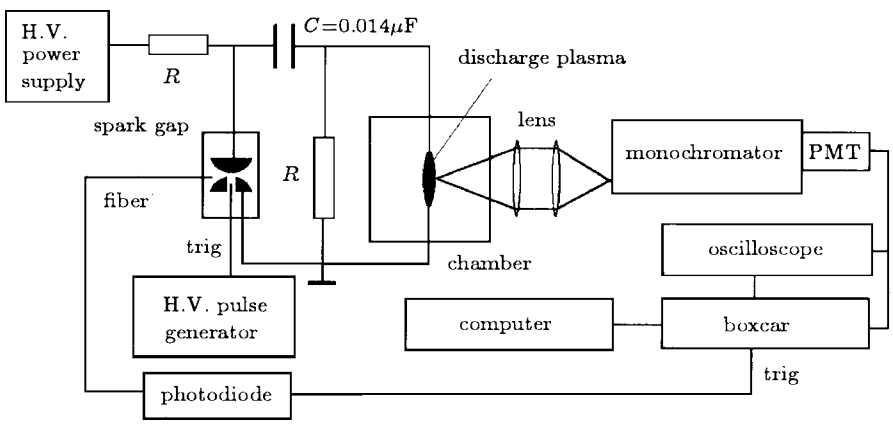


Fig.1. Pulsed discharge circuit and experimental set-up.

Optical emission spectroscopy was used to characterize the discharge plasma. The discharge plasma was imaged by two quartz lenses onto the entrance slit of a monochromator (BSO, WDP500-2A). The width of the entrance slit of the monochromator was about 150μm. The entrance slit was aligned at the centre of the plasma image. The spectral resolution of the monochromator is $\leq$0.1nm. The spectral signal was detected by a photomultiplier tube (PMT) (Hamamatsu, 1P28 or R712), and then averaged by a boxcar (Stanford, SRS250, 280). A digital oscilloscope (Tektronix) was used to monitor the spectral signal and the gate of the boxcar. The data from the boxcar were stored and processed by a computer. In order to minimize the synchronization error, the light emitted from the discharge in the spark gap was picked up by a fast photodiode (BPX-65) whose output was used to trigger the oscilloscope and the boxcar. Since the discharge is pulsed in our experiment, the spectra measured are time- and space-dependent. They vary with the gate width, delay time and the observation zone. The estimated transient temperature and the electron density are therefore the average values integrated with respect to time (gate width) and space (observation zone).

3. Results and discussion

3.1. Ammonia discharge spectrum

In the synthesis of nitrides with the help of continuous discharge, such as glow or arc discharge, few people choose ammonia as the working gas. This is because N_2 and H_2 would be generated during the discharge of NH_3, and the subsequently changed composition and pressure would affect the discharge stability.[13,14] Besides, the contaminant of hydrogen might be introduced into the synthesized materials. However, the problem of the unstable discharge can be solved by pulsed discharge because the pulsed discharge itself is a transient unstable process.

The emission spectra of ammonia discharge at 0.8 kPa were measured at a delay time of 300 ns. Emissions from N, N^+, H and NH were observed, as shown in Figs.2 and 3. No emissions of H_2, NH_2 and NH_3 were detected, indicating that the ammonia is highly dissociated. In these spectra, H emissions were much stronger than those from nitrogen (Fig.3) although the transition probabilities of H I lines are far

less than those of N II lines (as shown in Table 1), showing that the abundance of H atoms in the plasma is much higher than that of nitrogen atoms. This is in agreement with the composition of an ammonia molecule.

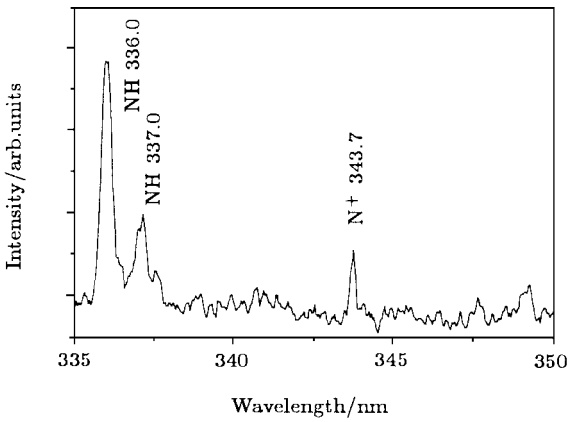


Fig.2. Emission spectrum from the discharge plasma of ammonia at 0.8kPa.

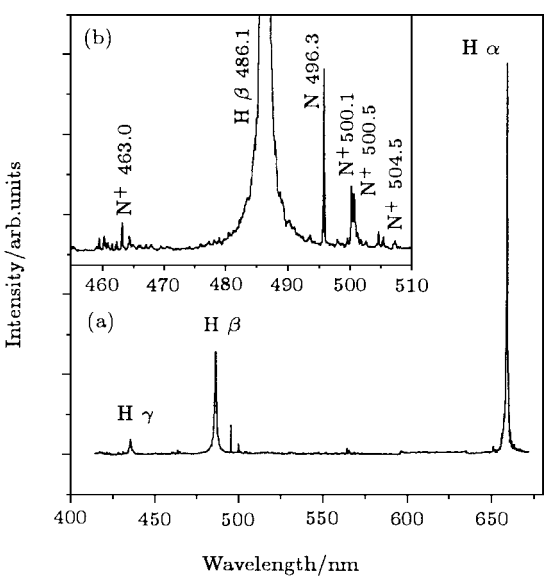


Fig.3. (a) H I Balmer lines in the emission spectrum of ammonia at 0.8kPa. (b) The enlarged spectrum in the neighbourhood region of the H β line.

Table 1. Transition probabilities for some lines of atomic hydrogen and nitrogen.

	Wavelength/nm	Transition probability/$10^8 s^{-1}$
H I	486.13	0.0842
N II	500.11	1.02
N II	500.15	1.08
N II	500.52	1.22
N II	504.51	0.410

In our previous work,[15] the features of the pulsed discharge of N_2 have been discussed in detail. Similar to the pulsed discharge of N_2, as the pressure was increased, more dissociation occurred and the emission from NH became weaker and the emissions from N^+ and H stronger. This is because, under higher pressures, the volume of the discharge plasma became smaller due to the shorter mean free path. Since the pulsed discharge energy is decided by the capacitance and the voltage supplied ($E = CV^2/2$), smaller discharge volume leads to a higher energy density. The increased energy density therefore causes more dissociation. However, in the case of ammonia discharge, this effect is not so obvious as in the nitrogen discharge.

For the purpose of generating atomic nitrogen in the discharge under lower pressures, a comparison between ammonia and nitrogen gas was made under the same discharge conditions (gas pressure of 0.8kPa and discharge voltage of 5.0kV). Their emission spectra are shown in Fig.4. The emission spectrum of NH_3 is entirely different from that of N_2. For nitrogen gas (Fig.4(a)), nearly all the major bands correspond to N_2. In contrast, in the discharge of ammonia, only emissions from N^+ were detected in the same spectral region (Fig.4(b)). The advantage of using ammonia at low pressures is obvious.

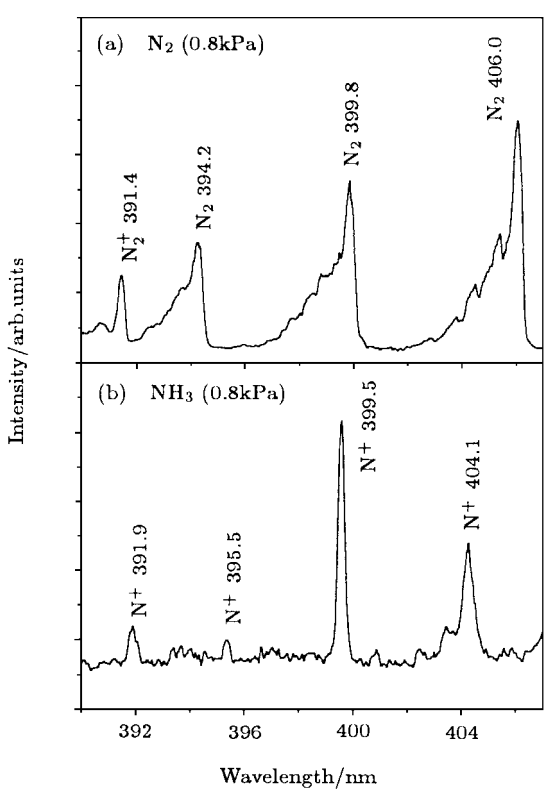


Fig.4. Emission spectra from the pulsed discharge of (a) N_2 and (b) NH_3 at the same pressure of 0.8kPa.

With the mechanism of the pulsed discharge, it is easy to understand the dissociation of NH_3 at low gas pressures. Compared with other types of discharge, the most peculiar character of the dc pulsed discharge is the huge current in the transient plasma. The discharge energy is from the charged capacitor, which is determined by the capacitance value and the voltage supplied. The shorter the pulse width, the higher the discharge current. In our experiment, we have found that the discharge pulse width is affected by the composition of the working gas. The discharge channel can be built easily by molecules with a lower ionization energy, such as NH_3, leading to a lower breakdown voltage, as described for the arc discharge of NH_3.[14] When NH_3 is used as the working gas, ions can be generated easily at the very beginning of the discharge. Once the discharge channel is built, free electrons are increased at avalanche speed, resulting in the shortening of the pulse and therefore a higher discharge current, which causes thorough dissociation of NH_3. Such a process is restricted in the discharge of N_2 due to its higher ionization energy.

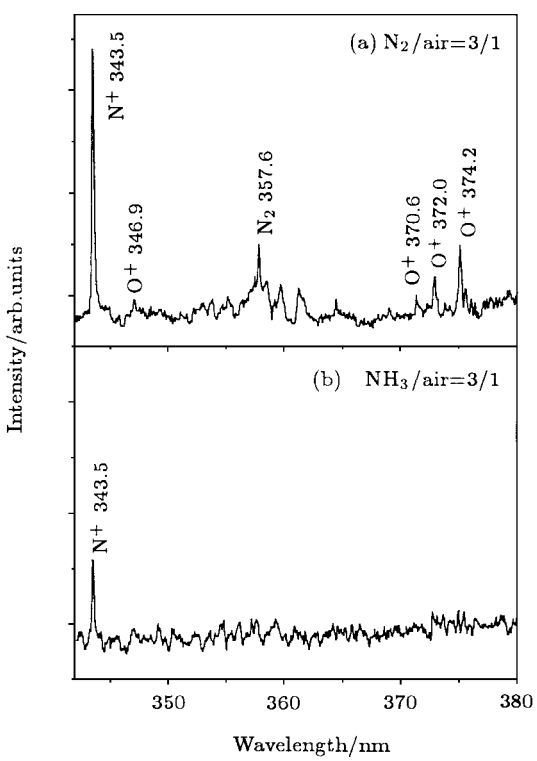


Fig.5. Emission spectra of (a) N_2/air and (b) NH_3/air mixtures with the same ratio of 3/1. The total pressure of the mixture is 4kPa.

It is known that many novel devices have been fabricated with GaN-based III nitrides. The device performance can, however, be limited by parasitic defect-induced emission such as the yellow luminescence observed in autodoped GaN.[16] Unintentionally doped GaN is generally strongly n-type primarily due to a high concentration of shallow donor Si_{Ga} and O_N.[16,17] Considering the high concentration of atomic hydrogen in the discharge plasma, the oxygen impurity might be eliminated by the reaction between hydrogen and oxygen. A test was made in our experiment by using the mixture of NH_3/air or N_2/air as the discharge gas. Figure 5 shows the emission spectra from the discharge of these mixtures, where the ratio of N_2 (or NH_3) to air is 3/1 and the total pressure is 4kPa. For the N_2/air mixture (Fig.5(a)), the major peaks correspond to N^+ and O^+ emissions, whereas no O^+ emission was detected in the discharge of the NH_3/air mixture (Fig.5(b)). The oxygen must react with the hydrogen generated in the discharge. This benefit of eliminating the oxygen impurities in the synthesis of nitride is especially useful for those precursors to be easily oxidized.

3.2. Excitation temperature and electron density of the plasma

The knowledge of the plasma temperature and electron density is helpful to the synthesis of materials or thin films. It is also important for the understanding of the dissociation, atomization, ionization, and excitation processes occurring in the discharge. In this paper, the excitation temperature and the electron density of the discharge plasma are investigated by emission spectroscopy.

The Boltzmann plot method is usually used to estimate electron excitation temperature from the corresponding intensity profiles in the spectrum. The method is based on the fact that the temperature is inversely proportional to the logarithm of the ratio of the intensities of lines arising from different upper levels, and proportional to the separation of excitation energy between any two of the lines. The spectral intensities measured in this experiment are line-of-sight values, measured by looking through the plasma from the side parallel to the centre line of the plasma.

The H-atom excitation temperature was estimated according to the relative intensities of H Balmer lines H α, H β and H γ at 434.0, 486.1 and 656.3nm, respectively, as shown in Fig.3. Since the discharge is pulsed, the estimated transient temperature and electron density are therefore the average values integrated with respect to time (gate width) and space (observation zone). The width and the delayed time

of the gate in Fig.3 are 900 and 300 ns, respectively. The width of the entrance slit of the monochromator is about 150μm. The entrance slit is aligned at the centre of the plasma image. A typical Boltzmann plot is shown in Fig.6. The lines in the plot are fitted to the data of the three H lines by least-squares regression. From the slope of the fitted lines, the temperatures are estimated to be about 3288 K for H atoms.

With the same method, the excitation temperature of N II is also estimated from the lines at 461.4, 462.1, 463.1 and 504.5nm, which is shown in Fig.7. The estimated temperature for N II is 3273K, very close to the temperature of H I.

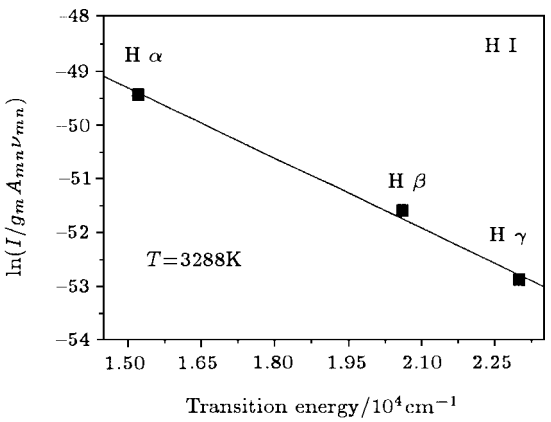


Fig.6. Boltzmann plot for the determination of the excitation temperature of H atoms in the discharge plasma of NH_3, where I is the emission intensity of the H Balmer line, g_m is the statistical weight of the energy level m, A_{mn} is the transition probability and ν_{mn} is the emission frequency. The straight line in the plot is the fitted line.

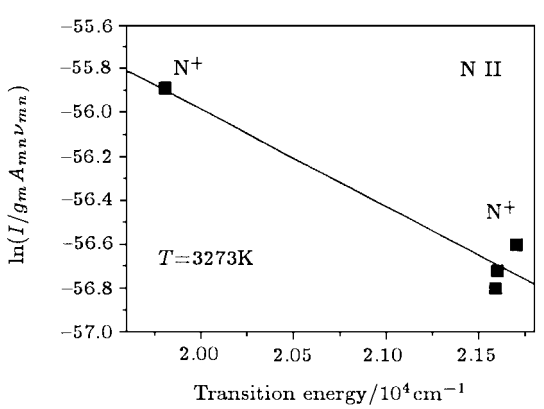


Fig.7. Boltzmann plot for the determination of the excitation temperature of N II in the discharge plasma of NH_3.

The electron density is also an important parameter for plasma. In the determination of the electron density, the Stark broadening profile is usually adopted. It is known that the calculated Stark broadening width for H β line has an accuracy of better than 5% as compared with the measured width.[18] The profile of the broadened H β line at 486.1nm is shown in Fig.8, where the width and the delayed time of the gate are 900 and 300ns, respectively. It should be noted that, in our experiment, according to the estimated temperature of the plasma, the thermal Doppler broadening of the H β line is negligible because it is far below the Stark broadening. Thus the electron density estimated from the half-width of the H β line in Fig.8 is about 1.7×10^{16}cm^{-3}.

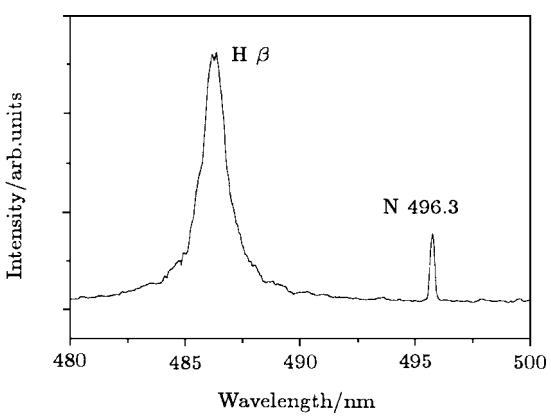


Fig.8. Stark broadening of the H β line in the discharge of NH_3 at 0.8kPa.

In the continuous dc arc discharge of NH_3 reported by Tahara *et al.*,[19] the excitation temperature and electron density of H atoms inside the jet are about 7000K and of the order of 10^{16}cm^{-3}, respectively. However, in our experiment, since the discharge is pulsed, the excitation temperature and the electron density are time-dependent. Table 2 lists a comparison of the excitation temperature and the electron density as a function of delay time, where the gate width is 300ns. We can see that the electron density decays much faster than the decay of temperature. This is due to the different mechanisms. The decay of excitation temperature is due to the expansion of the plasma as well as the energy transfer to the environmental gas. While for electron density, besides the expansion of plasma and the electron–ion recombination, the electrons are accelerated to the anode during the discharge. This process might be the reason of the fast decay of the electron density.

Table 2. A comparison of the excitation temperature and the electron density in the discharge plasma of NH_3 with different delay times.

Delay time/ns	T_e/K	n_e/cm^{-3}
50	4235	4.97×10^{16}
600	3058	1.32×10^{16}

4. Conclusion

In order to generate atomic nitrogen effectively under low gas pressures, the high-voltage pulsed discharge of NH_3 has been studied. Emission spectra show that ammonia is highly dissociated. More atomic nitrogen can be generated from NH_3 as compared to the discharge of N_2 at the same pressure of 0.8kPa. The excitation temperature and the electron density are time-dependent for a pulsed discharge. The estimated excitation temperatures of H I and N II are very close, which is about 3300K when the delay time is 300ns and the gate width is 900ns. The electron density of the discharge plasma is estimated to be of the order of 10^{16}cm^{-3} within 1.2μs after the discharge. The decay of the electron density is much faster than that of the excitation temperature.

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