

Detection of CN radicals in DC nitrogen plasma used for deposition of CN_x layers

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Abstract

Emission spectra from a DC plasma discharge of nitrogen with a graphite cathode used for deposition of CN_x layers were investigated in the visible range 350–900 nm. The spectra recorded at low and high resolution from both the negative glow and the positive column of the discharge were studied separately. All spectra are dominated by neutral and ionised N_2 emission. In the positive column the violet band of the cyanogen (CN) radical was identified and analysed for vibrational structure. From a computer simulation of the rotationally resolved violet band, vibrational temperatures were derived and found to be in the intensity distribution for the $v=0, 1$ and 2 levels from thermal equilibrium. In the negative glow the strong N_2^+ features completely mask the spectral region of the violet band of CN. Conclusions were drawn concerning the CN formation by chemical sputtering, and the role of CN radicals in the formation of polymeric CN_x layers of 1:1 = C:N stoichiometry. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

In laser ablation studies of carbon materials optical emission analysis is a commonly applied technique [1]. The process of CN_x layer formation in laser assisted ablation and deposition experiments or in various forms of low pressure dis-

charges is often monitored by the observation of light emission from the plasma [2–6]. A similar procedure was applied in this work for studying the DC glow discharge we have used in CN_x thin-film deposition.

The main purpose of this work is to follow the formation of the cyanogen (CN) radical in the discharge. The CN radical is one of the most thoroughly studied diatomic molecules; spectroscopic data is abundantly available for it [7]. Thus while it is important for the understanding of the

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physical and chemical processes leading to CN_x polymer formation as discussed in [2–6], it is also an ideal ‘thermometer’ to derive vibrational and rotational temperatures in plasmas. We shall discuss the general characteristics of the emission spectra, and shall derive temperatures using a diatomic spectroscopic simulation program [8].

2. Experimental

A glow discharge was created in a reactor made of glass (with overall dimensions of $\varnothing 2 \times 15$ cm) used for deposition of CN_x layers (Fig. 1), employing a graphite cathode, and a silicon wafer on an aluminium anode for the collection of the CN_x deposited from the plasma as described in detail in [9,10]. The voltage applied to the electrodes was in the range of 400–800 V, and the current range was 2–40 mA, depending on gas pressure, composition and the applied voltage. The pressure was set to 2.7 mbar of flowing N_2 in a dynamic vacuum. For studies of the N_2 discharge without the carbonaceous species an Al cathode was applied. The purity of N_2 gas was 4N throughout these experiments.

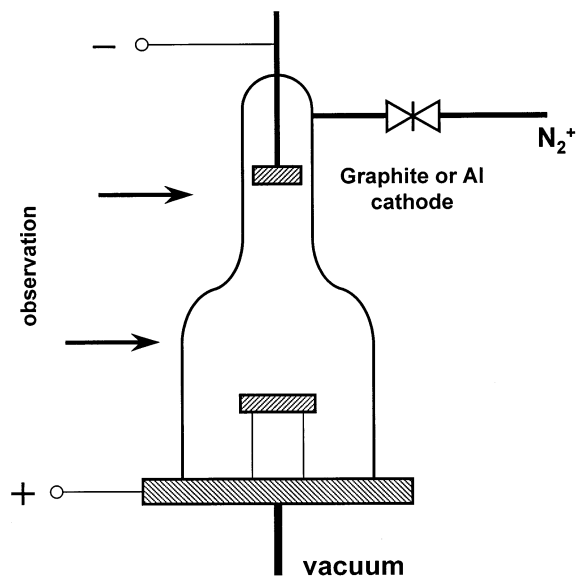


Fig. 1. The scheme of the DC plasma reactor for CN_x deposition.

Low-resolution spectra were recorded with an Ocean Optics S2000 fiber-optic spectrometer in the visible range. The optical resolution was 1.5 nm. Spectra were both statically and dynamically averaged using the OOIBase software.

High-resolution spectra were collected on a Carl Zeiss PGS-2 (Jena) planar grating spectrograph in the 1st order, equipped with an EMI 6256B photomultiplier (200–600 nm). The optical resolution was varied between 0.2 and 0.04 nm.

Spectra were recorded perpendicularly to the vertically positioned reactor axis in the vicinity of the cathode. Spectral data was recorded from the positive column of the discharge by either appropriately positioning a small quartz lens equipped with a fiber optic at the entrance opening or by using a quartz lens for imaging the appropriate part of the discharge to the entrance slit of the spectrograph.

To identify features as a result of carbon containing molecules, comparisons were made between spectra taken with aluminium and carbon cathodes under otherwise identical conditions.

3. Results

3.1. Emission spectra of N_2 discharge

The low-resolution emission spectrum of nitrogen at 2.7 mbar recorded in the negative glow area is shown in Fig. 2. A similar spectrum obtained from the positive column of the pure nitrogen discharge is seen in Fig. 3. Both spectra are dominated by molecular nitrogen emission. In the negative glow region the N_2^+ ion has the strong first negative system (B–X), covering the spectral range 350–500 nm, and a similar strong emission at longer wavelengths, as a result of the first positive system (B–A) of neutral N_2 . The positive column has a much weaker intensity (the spectrum in Fig. 3 was collected for 500 ms, while for Fig. 2 the collection time was 100 ms), and the short wavelength region is dominated by the second positive system (C–B) of neutral N_2 . There is a large quantity of papers dealing with optical emission from nitrogen under plasma conditions, eg. [11].

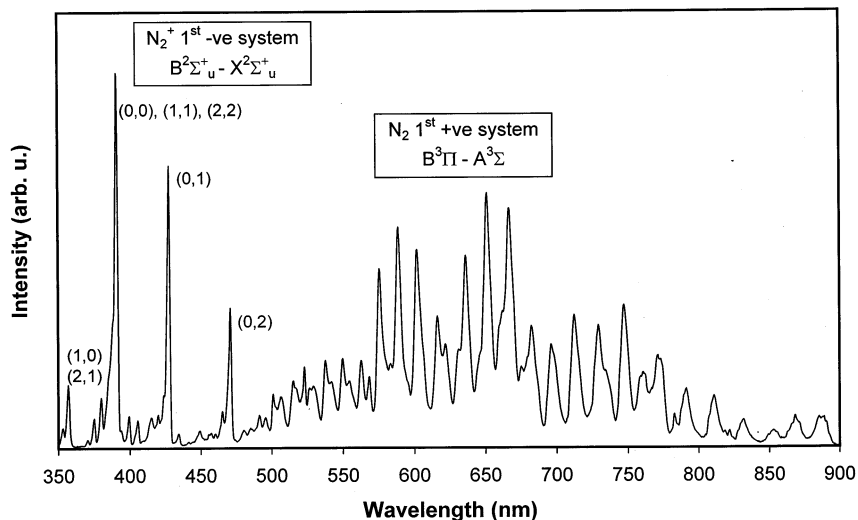


Fig. 2. Low resolution spectrum of the negative glow area.

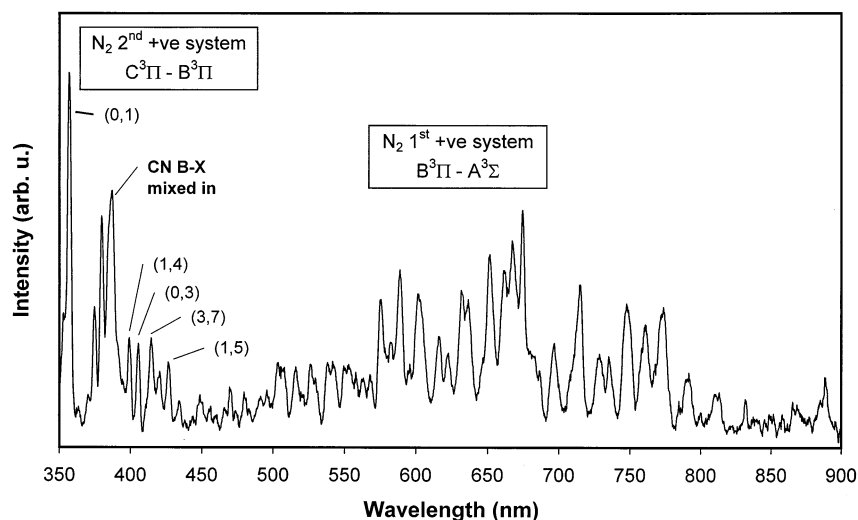


Fig. 3. Low resolution spectrum of the positive column area.

3.2. Emission spectra of N_2 -graphite discharge

The B–X violet system of neutral cyanogen in the positive column emission, where the overlap with the C–B band of neutral N_2 is minimal, was studied. In the negative glow the strong B–X system of N_2^+ (this molecule is isoelectronic with CN) almost completely masks CN emission at the available resolution. The possibility of observing

the different spatial regions of the plasma is unique in this kind of DC plasma arrangement and we have found no references in recent CN_x deposition literature applying this arrangement. The CN violet band has also been studied in reactive laser ablation experiments at low spectral resolution. However, under such conditions it is easy to assign N_2 emission to the CN feature [12].

The B–X violet band of cyanogen is located

between 355 and 425 nm [7,8] in the spectrum shown in Fig. 3, with a strong feature at around 390 nm, containing the $\Delta v = 0$ vibrational progression. Both the $\Delta v = -1$ and $\Delta v = +1$ progressions at approximately 325 and 425 nm, respectively, are much weaker than in the negative glow and the identification of them in the nitrogen plasma environment is difficult.

In Fig. 4 the high-resolution spectra of the positive column emission is shown, recorded with both the Al and graphite cathodes. The plasma excitation and spectral recording parameters for the two spectra were otherwise identical. The B–X band of CN is unambiguously detected in the 382.5–390 nm region. This band is embedded in clearly resolved vibrational progressions of the C–B system of neutral N_2 . The nitrogen spectrum of the positive column presents only a small interference with the B–X band. The only exception is the weak vibrational feature at about 386 nm; the (4,7) progression member. The numbering above the members of the vibrational progressions refers to the C and B state vibrational quantum numbers for N_2 . The noise level of the observed spectrum in Fig. 4 does not allow for clear identification of the rotational structure. As a result of this noise the extra spectral features (before the (0,0) band) could not be assigned to a particular molecule.

In order to estimate vibrational and rotational temperatures for the cyanogen molecule the rotational structure has to be resolved. Fig. 5 shows a narrow spectral range resolving rotational features. The three P-band heads of the (0,0), (1,1) and (2,2) vibrational members of the progression are clearly seen, the rotational structure is evident and is clearest between 385 and 387 nm. Higher diagonal vibrational progressions are much weaker and cannot be identified with certainty. Using the spectral simulation program LIFBASE [8] calculations for the closest fit to the experimental data were carried out. The result of a typical simulation calculation is given in Fig. 6.

The generally good agreement between the calculated and observed spectra is a convincing proof that the cyanogen radical has indeed been observed. In addition the ratio of the intensities of the P-band heads for the strong (0,0), (1,1) and (2,2) vibrational does not correspond to thermal equilibrium. In the latter case the (1,1) band and especially the (2,2) band should have smaller intensities corresponding to a smaller vibrational population. In the simulation the vibrational temperature was set to 3500 K, and in order to reproduce the experimental relative intensity, an non-Boltzmannian population distribution was applied. Setting the vibrational population unity

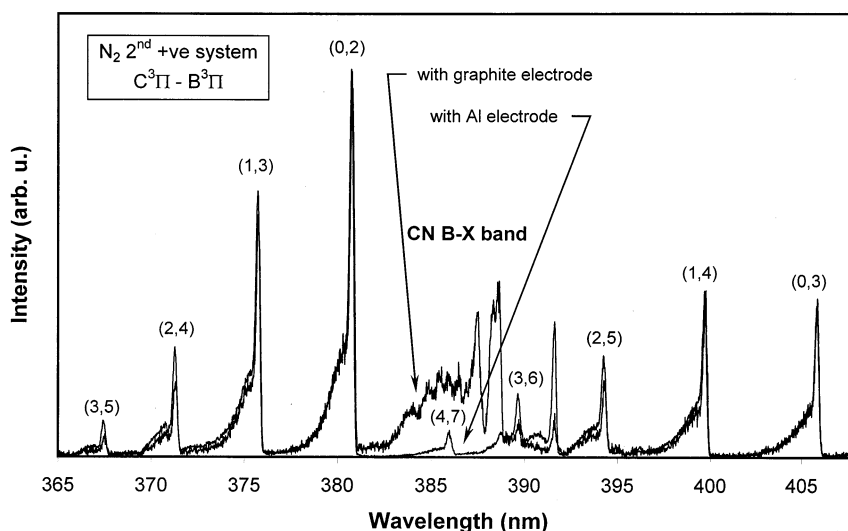


Fig. 4. Comparison of high resolution spectra of the positive column for graphite and aluminium cathodes.

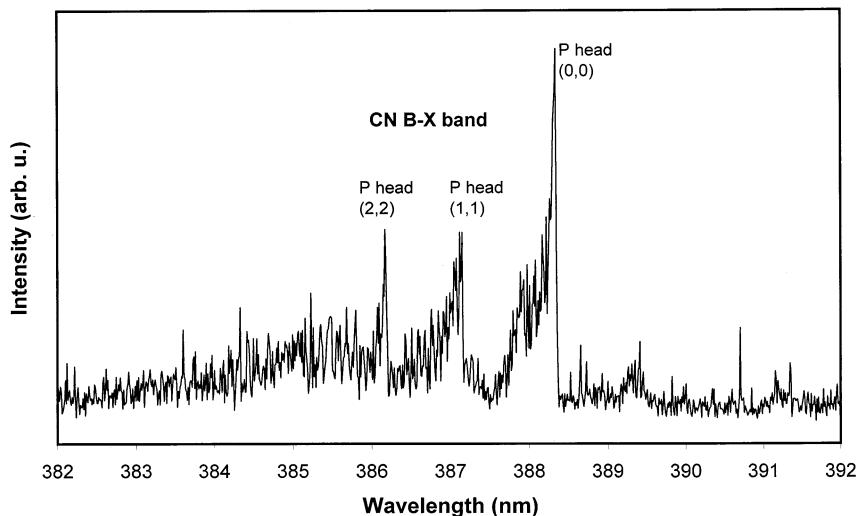


Fig. 5. High resolution spectrum of the $\Delta v = 0$ part of the CN violet band.

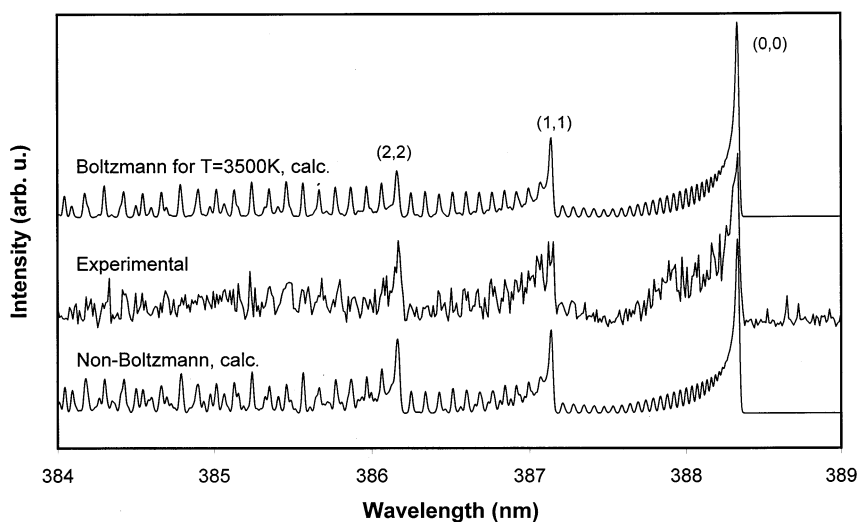


Fig. 6. Simulation of the B–X band of CN compared to the experimental spectrum.

for the $v = 0$ level, for a close simulation a relative population of 0.49 for the $v = 1$ and $v = 2$ levels was used. This value differs by factors 1.16 and 2.74 from thermal equilibrium values for $v = 1$ and $v = 2$ states.

The rotational temperature was assumed to be also 3500 K. This is a weak assumption as, rotational temperatures higher than vibrational ones are equally compatible with the experimental

spectrum. We have no particular model for rotational and vibrational excitations in our plasma, thus this problem calls for further experiments and analysis.

In discharge plasmas involving carbon electrodes it would be obvious to look for the C_2 radical. We have searched for the Swan bands of C_2 ($d^3\Pi_g - a^3\Pi_u$) that are expected to appear in five vibrational progressions: $\Delta v = -1, +1, 0$,

– 2, + 2 (see, eg. in [5]) between 430 and 600 nm. In laser-induced plasmas the $\Delta v = 0$ and + 1 progressions are usually strong around 517 and 474 nm. None of our low-resolution spectra showed these features, although in Fig. 2. The (0, 2) peak in the B–X system of N_2^+ could possibly mask the $\Delta v = + 1$ bandhead of C_2 . In Fig. 3 the positive column spectrum is completely lacking in C_2 features.

Theoretically it would be possible to find three- and four atomic molecules, formed of carbon and nitrogen in our plasmas, such as dicyanogen (C_2N_2), and the radicals CNN, NCN or CCN. In any case their known electronic spectra [13,14] tends to appear in the far ultraviolet but it was not covered in the present paper. Detection of these important species thus remains for further work.

4. Discussion

There appears to be three fundamental chemical problems connected with the plasma synthesis of CN_x layers: (1) the mechanism of the formation of C-containing species (eg. CN radicals); (2) the chemical processes taking place in the plasma; and (3) the build-up of the solid CN_x product from its gas-phase precursors.

Our studies so far are in complete accord with previous studies [1–6], in as much as CN_x layers must be forming from the cyanogen content of the plasma. There is no doubt that CN is present in the positive plasma column, and it probably also occurs in the negative glow. The lack of observation of C_2 suggests that CN formation occurs right on the surface of the graphite cathode, in a gas-solid phase reaction between the active N_2 and N_2^+ molecules and the carbon material, either precluding C_2 formation or involving an immediate conversion of C_2 into CN. This is in contrast to conditions prevailing in laser-induced plasmas where C_2 is observed along with CN in the gas-phase [6]. In our case bombardment of the graphite target by N_2^+ accelerated in the applied electric field ('cathode fall') generates the CN species at the outermost atomic layers of the target.

Although it is possible that larger molecules, such as C_2N_2 are formed in the plasma from CN and are directly contributing to CN_x formation, we have not been able to detect such species. We surmise that they are in very low concentration in the plasma and would need much more sophisticated experiments for a spectroscopic study. We have obtained solid evidence that at the applied conditions 'stoichiometric' CN layers are formed as detected by in situ XPS investigations of the composition in various stages of the deposition process [9,10].

In the near future we plan to study the effects of rare gases, especially that of He, and the effect of hydrogen upon CN_x formation in the plasma reactor. This might shed some light on the excitation mechanisms prevailing in DC carbon–nitrogen plasmas and help understanding the formation of CN polymers.

5. Conclusion

- The presence of the CN radical in the N_2 plasma with the graphite cathode was clearly established.
- A unique identification of the CN radical in the violet band was obtained by resolving the rotational structure, and the vibrational temperature was estimated.
- Non-thermal vibrational population distribution was deduced for the B–X electronic transition of CN by spectral simulation.
- Formation of CN_x layers in DC plasma from CN radicals acting as precursors is supported by the relatively stable 1:1 'stoichiometry' of the deposited materials.

Acknowledgements

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References

- [1] Y. Tasaka, M. Tanaka, S. Usami, *Appl. Surf. Sci.* 79–80 (1994) 141.
- [2] Y. Tasaka, M. Tanaka, S. Usami, *Jpn. J. Appl. Phys.* 34 (1995) 1673.
- [3] G. Dinescu, E. Aldea, P. Boieriu, G. Musa, A. Andrei, M. Dinescu, G.J.H. Brussaard, R.J. Severens, M.C.M. van de Sanden, D.C. Schram, *Nucl. Instr. Meth. B* 120 (1996) 298.
- [4] C. Jama, V. Rousseau, O. Dessaux, P. Goudmand, *Thin Solid Films* 302 (1997) 58.
- [5] S. Acquaviva, A.P. Caricato, M.L. De Giorgi, A. Luches, A. Perrone, *Appl. Surf. Sci.* 46 (1997) 408.
- [6] E. Aldea, A.P. Caricato, G. Dinescu, A. Luches, A. Perrone, *Jpn. J. Appl. Phys.* 36 (1997) 4686.
- [7] K.P. Huber, G. Herzberg, *Molecular spectra and molecular structure, IV. Constants of diatomic molecules*, in: W.G. Mallard, P.J. Linstrom (Eds.), *NIST Chemistry WebBook*. NIST Standard Reference Database Number 69, National Institute of Standards and Technology, 1998.
- [8] J. Luque, D.R. Crosley, *LIFBASE*, Database and Spectral Simulation for Diatomic Molecules, SRI International, Menlo Park, CA, USA, 1999.
- [9] I. Bertóti, M. Mohai, A. Tóth, B. Zelei, *Nucl. Instr. Meth. B* 148 (1999) 645.
- [10] M. Mohai, I. Bertóti, A. Tóth, B. Zelei, *Surf. Interface Anal.* (2000) in press.
- [11] N. Xu, Y. Du, Z. Ying, Z. Ren, F. Li, J. Lin, Y. Ren, X. Zong, *J. Phys. D: Appl. Phys.* 30 (1997) 1370.
- [12] E. D'Anna, A. Luches, A. Perrone, S. Acquaviva, R. Alexandrescu, I.N. Mihailescu, J. Zemek, G. Majni, *Appl. Surf. Sci.* 106 (1996) 126.
- [13] G. Herzberg, *Molecular spectra and molecular structure III*, in: *Electronic Spectra and Electronic Structure of Polyatomic Molecules*, Van Nostrand, Princeton, NJ, 1966.
- [14] H. Okabe, *Photochemistry of Small Molecules*, Wiley, New York, 1978.