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Optical emission spectroscopy study for nitrogen–acetylene–argon and nitrogen–acetylene–helium 100 kHz and dc discharges

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ABSTRACT

The optical emission spectroscopy was applied to investigate the middle frequency (100 kHz) and dc low pressure discharges, generated in the nitrogen–acetylene–argon and nitrogen–acetylene–helium mixtures, commonly used for deposits of carbon nitride thin layers. Changes in the emission intensities of the selected species: CN, CH, C, H, N_2, N_2^+ as well as Ar, Ar^+ and He, were studied as a function of the discharge current. Excitation processes occurring in the presence of argon and helium were compared and discussed. The N_2–C_2H_2–Ar and N_2–C_2H_2–He plasmas generated in the 100 kHz and dc glow discharges were characterized by the excitation (Ar, He, H), vibrational (CN, N_2) and rotational (CN, N_2^+) temperatures. A significant deviation from the equilibrium state was observed for the plasma containing argon as well as helium.

1. Introduction

The study of hydrocarbon–nitrogen mixtures with and without noble gases (argon, helium, neon, xenon, krypton) and low pressure discharges is of great importance due to their wide application in production of carbon nitride materials [1–10]. Usually, for the deposition of carbon nitride thin layers (CN:H) by the plasma-assisted chemical vapour deposition (PACVD) method, methane–nitrogen [2,6,7] or acetylene–nitrogen [1,8,9] mixtures at various molecular gas ratios were applied. The quality and properties of the carbon nitride coatings strongly depended on the deposition conditions [9]. It was reported [11,12] that an addition of the noble gases to the hydrocarbon–nitrogen plasma changed the microstructure of the carbon nitride thin layers and, consequently, their properties.

In order to understand the mechanism leading to the formation of materials with relevant parameters, it is necessary to investigate plasma parameters and phenomena which occur in the plasma phase. The reaction occurring in the gas plasma phase as well as concentrations of active species play a key role in the processes leading to the formation of thin layers.

The optical emission spectroscopy (OES), due to its non-invasive character was often applied to investigating and controlling plasma processes [13–15]. It yields information about the excited species in the plasma, the plasma processes as well as the plasma temperatures [13–18]. The optical emission spectroscopy was often employed to investigate the reactive plasma system enabling to the formation of coatings and films [7,17,19]. However, knowledge on plasma characteristics for the system containing acetylene, nitrogen and noble gases is very scarce [20,21]. The interaction of noble gases (Ar, He, Ne, Xe, Kr) plasmas with carbon nitride coatings was investigated by Durrant et al. [20] by means of OES. They recorded and identified species present in plasma spectrum and found that low concentration of CH was produced as a result of an interaction of noble gases with CN:H materials. The optical actinometry techniques, based on the emission intensity measurements, were also applied to the study of acetylene–nitrogen–helium radio frequency plasma [21]. Sung et al. [12] showed that an addition of argon to the acetylene – nitrogen microwave plasma significantly enhanced the emission intensity of CN radical. Dinescu et al. [22] studied a low pressure arc generated in the acetylene–nitrogen–argon mixture by the OES technique to know mechanism of chemical reactions.

Previously [16], we investigated the middle frequency (100 kHz) and direct current (dc) plasmas generated in the nitrogen–acetylene mixtures, using OES and the optical actinometry technique. Here, the effect of the addition of noble gases (Ar or He) to the nitrogen–acetylene 100 kHz and dc plasma was analyzed versus the discharge current. The plasma parameters, i.e. electron "excitation", vibrational and rotational temperatures were determined and compared for dc and the 100 kHz plasma.

2. Experimental setup

The experimental setup was described in the earlier works [16,19]. Briefly, the middle frequency (100 kHz) or direct current

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(dc) discharge was generated between two parallel Armco steel electrodes (diameter 22 mm, thickness 2 mm, space between the electrodes 16 mm) in a Pyrex glass chamber. The plasma reactor contained the quartz window enabling observation of the plasma radiation between the electrodes. The reactor walls were cooled by tap water. The JY Triax 320 monochromator (resolution 0.05 nm in the first order for diffraction grating with 1200 grooves mm^{-1}) and the PGS-2 spectrograph (resolution 0.012 nm for diffraction grating with 651 grooves mm^{-1}) working with photomultipliers (Hamamatsu R-928 or DH-3), were applied here to record spectra. The changes of all optical system sensitivities versus the wavelength (from 200 to 800 nm) were corrected by means of the CL2 Bentham Reference Lamp. The UV achromatic lens ($f = 80$) were used to focus the plasma radiation on the entrance slit of the spectrometer or the spectrograph. The radiation of plasma was collected near the cathode in the negative glow region.

The gas mixtures flowing through the glass chamber were pumped continuously using the rotational pump with the cryogenic trap (liquid nitrogen). The pressure gauge (Pfeiffer PKR 251) was applied here to control the chamber pressure. During all the experiments, the pressure was maintained at 6 Torr (800 Pa). The gases used, i.e.: acetylene, nitrogen, argon and helium, were 99.99% grade pure. The N_2:C_2H_2:Ar(He) ratio was 1:1:1 for each measurement.

The current was varied in the range from 60 to 120 mA for the dc and 100 kHz discharges. The operating powers of both discharges were the same. The current increase in the discharges from 60 to 120 mA caused the growth of the voltage from 500 V to 700 V and from 700 V to 985 V for the N_2–C_2H_2–Ar and N_2–C_2H_2–He mixtures, respectively.

3. Results and discussion

3.1. Emission intensities of species in the N_2–C_2H_2–Ar and N_2–C_2H_2–He mixtures

The emission spectra of 100 kHz and dc discharges in the argon–nitrogen–acetylene and nitrogen–acetylene–helium mixtures were measured in the range of wavelength from 200 to 800 nm. The main species observed in the N_2–C_2H_2–Ar and N_2–C_2H_2–He discharges were: N_2^+, N_2, CN, H, CH, NH and C. The same species were noted in the acetylene–nitrogen plasma [19]. Additionally, in the mixture containing argon numerous Ar I lines with the excitation energy from 13 to 15.5 eV and Ar II lines (excitation energies 19–22 eV, total excitation energies from 35 to 38 eV) were detected. When, helium was introduced, instead of argon, to the acetylene–nitrogen plasma several atomic lines of He I were observed. The most intensive lines of He I were noted at 388.86; 447.15; 501.57; 587.56 and 667.81 nm. The He I line at 388.86 nm was partially overlapped by the (0–0) band of N_2^+ with the band head at 391.44 nm. No ionized helium lines could be recorded, due to high ionization energy of helium (24.58 eV). Intensities of Ar I and ArII lines were considerably higher in the 100 kHz plasma in comparison to those in the dc plasma. A similar effect was observed for He I lines, which were more intensive in the 100 kHz discharge. Generally, the increase of current caused the growth of emission intensities of Ar I, Ar II and He I in the N_2–C_2H_2–Ar and N_2–C_2H_2–He mixtures, respectively. Emission spectra of the N_2–C_2H_2–Ar and N_2–C_2H_2–He plasma were compared in Fig. 1.

The following species: CH, CN, C, H, N_2^+ and N_2, may play an important role in the plasma processes leading to the formation of carbon nitride materials and thus the emission intensities of these species were monitored versus the discharge current. The lines and molecular bands of the species as well as their spectroscopic data were presented in the Table 1.

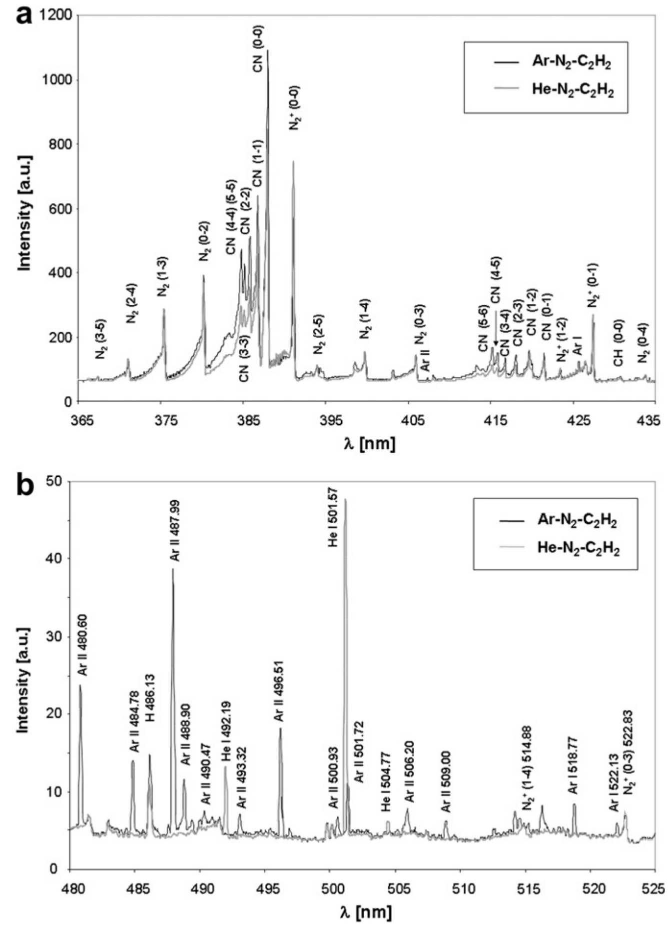

Fig. 1. The emission spectra of the N_2–C_2H_2–Ar and N_2–C_2H_2–He mixtures in the region a) from 365 to 435 nm and b) from 480 to 525 nm.

The variations of the emission intensities of H, CH, CN and C versus the discharge current are shown in Figs. 2 and 3 for the 100 kHz and dc plasmas. The change of the current from 60 to 120 mA led to an increase in the intensities of H, CH, CN and C in the both analyzed mixtures and discharges. In the 100 kHz as well as dc discharges, the intensities of H, CH and CN radicals were higher than in the case of the N_2–C_2H_2–Ar mixture.

Cracking the C–H bond in the acetylene (H–C≡C–H) molecule by the electron impact is probably a first fragmentation step, because the energy of the C≡C bond (10 eV) is higher than the energy of the C–H bond (5.8 eV) in acetylene [22].

$$C_2H_2 + e = C_2H + H + e \quad (1)$$

The C_2H radical may be then dissociated to the CH molecule and the H atom as a result of impact with argon ions [23]. On the other hand, the metastable states of argon with the energies of 11.55 eV Ar($^3P_2$) and 11.72 eV Ar($^3P_0$) in the N_2–C_2H_2–Ar mixture may also contribute

Table 1
List of the investigated species.

Species	Wavelength [nm]	Transition	Threshold energy [eV]
H	656.28	$3d^2\ (D_{3/2})$–$2p^2P^o{}_{3/2}$	12.1
C	247.86	$3s^1\ (P^o)$–$2p^2\ (^1S)$	7.68
CH	431.44	(0–0) $A^2\Delta$–$X^2\Pi$	2.9; ∼ 11
CN	388.43	(0–0) $B^2\Sigma$–$X^2\Sigma$	3.2
N_2	380.49	(0–2) $C^3\Pi_u$–$B^3\Pi_g$	11.2
N_2^+	391.44	(0–0) $B^2\Sigma^+{}_u$–$X^2\Sigma^+{}_g$	3.1; 18.7