Spectroscopic study of the decomposition process of tetramethylsilane in the N_2–H_2 and N_2–Ar low pressure plasma

P. Jamroz, W. Zyrnicki[*]

*Institute of Inorganic Chemistry and Metallurgy of Rare Elements, Chemistry Department, Wroclaw University of Technology,
Wyb. Wyspianskiego 27, 50-370 Wroclaw, Poland*

Abstract

The optical emission spectroscopy has been used to study the decomposition process of tetramethylsilane in a low pressure plasma. The $Si(CH_3)_4$–N_2–H_2 and $Si(CH_3)_4$–N_2–Ar reactive mixtures, which are used for the deposition of SiCN layers, have been studied here. High energy active species were identified in the plasma phase and the electron excitation, vibrational and rotational temperatures as well as electron number density were determined for various compositions of the reactive mixtures. The electron excitation temperature (Si I, Ar I, H) was found to be higher than the vibrational temperatures (CN, N_2, N_2^+) and considerably higher than the N_2^+ rotational temperature, as the results of nonequilibrium state of plasma generated. It was observed that introduction of tetramethylsilane as well as growth of hydrogen percentage led to lowering of the electron density and the rotational temperature. Optical actinometry was applied to study the $Si(CH_3)_4$–N_2–H_2 reactive mixture.
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1. Introduction

Plasma techniques, e.g. plasma assisted chemical vapour deposition (PACVD), are often employed for production of a great variety of coatings and thin layers [1]. The structure and composition of the layer manufactured by PACVD methods strongly depend on plasma parameters. Thus, the knowledge of plasma parameters is very important for investigation of layer deposition processes. The plasma parameters, such as temperature (rotational, vibrational, excitation) and electron number density, are usually used for characterization of plasma. These parameters are fundamental both for understanding plasma processes and for description of plasma nonequilibrium or equilibrium states. Emission spectroscopy methods have been employed for determination of temperature in various types of plasmas (see, e.g. [2–6]). The electron density has been measured by Langmuir probe (invasive method) [7] and by non-invasive spectroscopic approach [8,9].

The synthesis of silicon carbon nitride (SiCN:H) layers by PACVD methods has attracted a great interest in recent years, due to unique properties of the SiCN materials, among them: high hardness, low friction, resistance to high temperature and anticorrosive [10,11]. A mixture of N_2, H_2, CH_4 and SiH_4 was often used for production of silicon carbon nitride coatings [12,13]. However, the mixture containing SiH_4 is potentially dangerous. Very recently, easy volatile organosilicon compounds, e.g. tetramethylsilane (TMS: $Si(CH_3)_4$), hexamethyldisilazane (HMDSN: $(CH_3)_3SiNSi(CH_3)_3$), were found to be very promising to fabricate SiCN layers [11,12,14]. These precursors may be used as a simultaneous source of carbon and silicon at strictly specified molar ratio.

A great attention has been devoted to investigation of the deposition process of SiCN [6,7,15]. However, only a

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* Corresponding author. Tel.: +48 71 3202494; fax: +48 71 3284330.
E-mail address: wieslaw.zyrnicki@pwr.wroc.pl (W. Zyrnicki).

few papers reported spectroscopic studies of the process of the silicon carbon nitride production [7,13,16–18]. Very recently Welzel et al. [7] investigated the Si, CH, H concentrations in the argon–nitrogen–TMS microwave low pressure plasma and determined electron number density and electron temperature using Langmuir probes. Barbadillo et al. [13] studied emission spectra emitted by SiH_4–N_2–CH_4–Ar microwave plasma and identified high energy species in the plasma phase. The identification of active species in the SiH_4–N_2–H_2 plasma with addition of gaseous organic compounds (CH_4, C_2H_2 and CH_3NH_2) was also carried out by Wu et al. [15]. They noticed that production of active carbon species was crucial for the SiCN layer growth. The N_2–H_2 low pressure plasma with addition of CH_3SiCl_3 was studied by means of optical emission spectroscopy and actinometry technique [16]. They observed that the growth of nitrogen concentration in the N_2–H_2–CH_3SiCl_3 mixture caused enhanced production of CN and CH radicals. The decomposition process of $SiCl_4$ in the N_2–C_2H_2 plasma was also investigated and the rotational and excitation temperatures were determined [17]. In addition to those systems examined with respect to the SiCN layers, very recently, the Ar–SiH_4–CH_4 inductively coupled plasma was studied by optical emission spectroscopy and the Ar I excitation and gas temperatures were determined [2]. Raymond et al. [18] reported measurements of the ground state species in the tetramethylsilane decomposition process by IR spectroscopy.

In this paper optical emission spectroscopy was applied to investigate the decomposition process of TMS in the nitrogen–hydrogen and nitrogen–argon 100 kHz low pressure plasma. The tetramethylsilane was used here as a single source of carbon and silicon. The plasma containing $Si(CH_3)_4$ was characterized by means of electron excitation, vibrational and rotational temperatures as well as electron number density. Additionally, the optical actinometry technique was used to determine the relative concentration of species in the N_2–H_2–$Si(CH_3)_4$ mixture. Effect of argon or hydrogen contribution on decomposition of tetramethylsilane was examined.

2. Experimental procedures

A schematic diagram of the experimental reactor is shown in Fig. 1. The plasma was generated between two parallel Armco-steel electrodes in the Pyrex glass chamber. An alternating current (100 kHz) power supply (maximum power 200 Watt) was applied to excite plasma. The electrode diameter and distance between the electrodes were 22 and 16 mm, respectively. The central part of cylinder reactor was equipped with quartz window. The radiation of plasma was recorded by means of JY TRIAX 320 monochromator (focal length 32 cm) and by high resolution PGS-2 spectrograph (focal length 200 cm) equipped with an electronic and computerized measurement system. Spectra emitted by plasma were focused on monochromator or spectrograph entrance slit by means of achromatic lens ($f = 180$). The optical signal was detected with the aid of photomultiplier tube (Hamamatsu R-928 or Hamamatsu DH-3). The total optical system, including variation of photomultipliers sensitivity versus wavelength, was calibrated by means of the Bentham CL2 lamp using the Protection Engineering LTD certificate. The spectra were recorded near the "cathode" (powered electrode) (above 2 mm from cathode). The nitrogen–hydrogen or argon–nitrogen was used as a carrier gas. The fraction of nitrogen in the reactive mixture, i.e. nitrogen–hydrogen or nitrogen–argon, was varied over the range of 0 to 100%
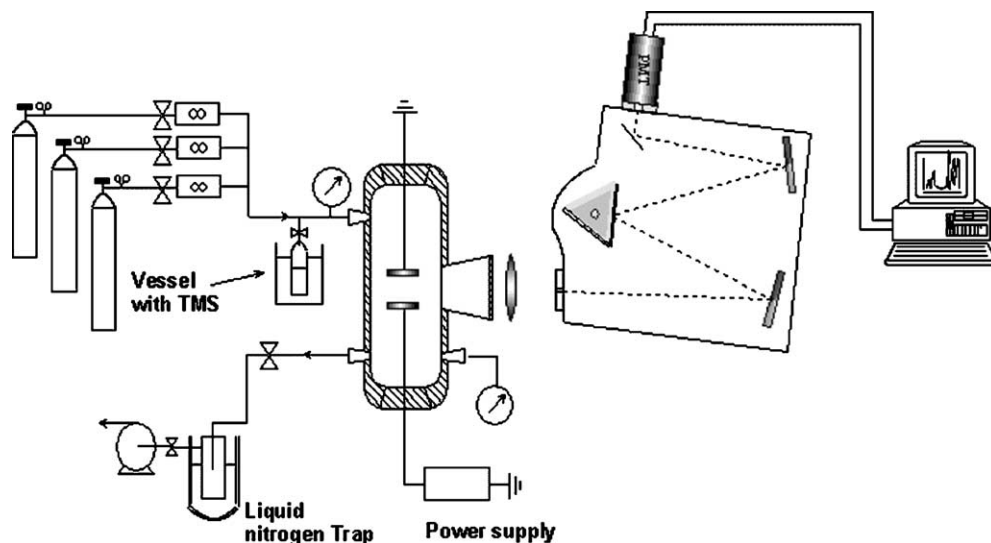

Fig. 1. Schematic diagram of the experimental setup.

(partial pressure ratio), with the step of 25%. Tetramethyl-silane (Aldride made, 99.9% purity) cooled in ice-water bath was introduced with the stream of gases to the plasma zone by means of Teflon-valve system. The experiment was carried out at the following conditions: total pressure 4 Torr (530 Pa), the flow rate of TMS 0.04 g min^{-1} and the current of discharge 100 mA. The cryogenic trap in front of the pump was employed in order to avoid possible contami-
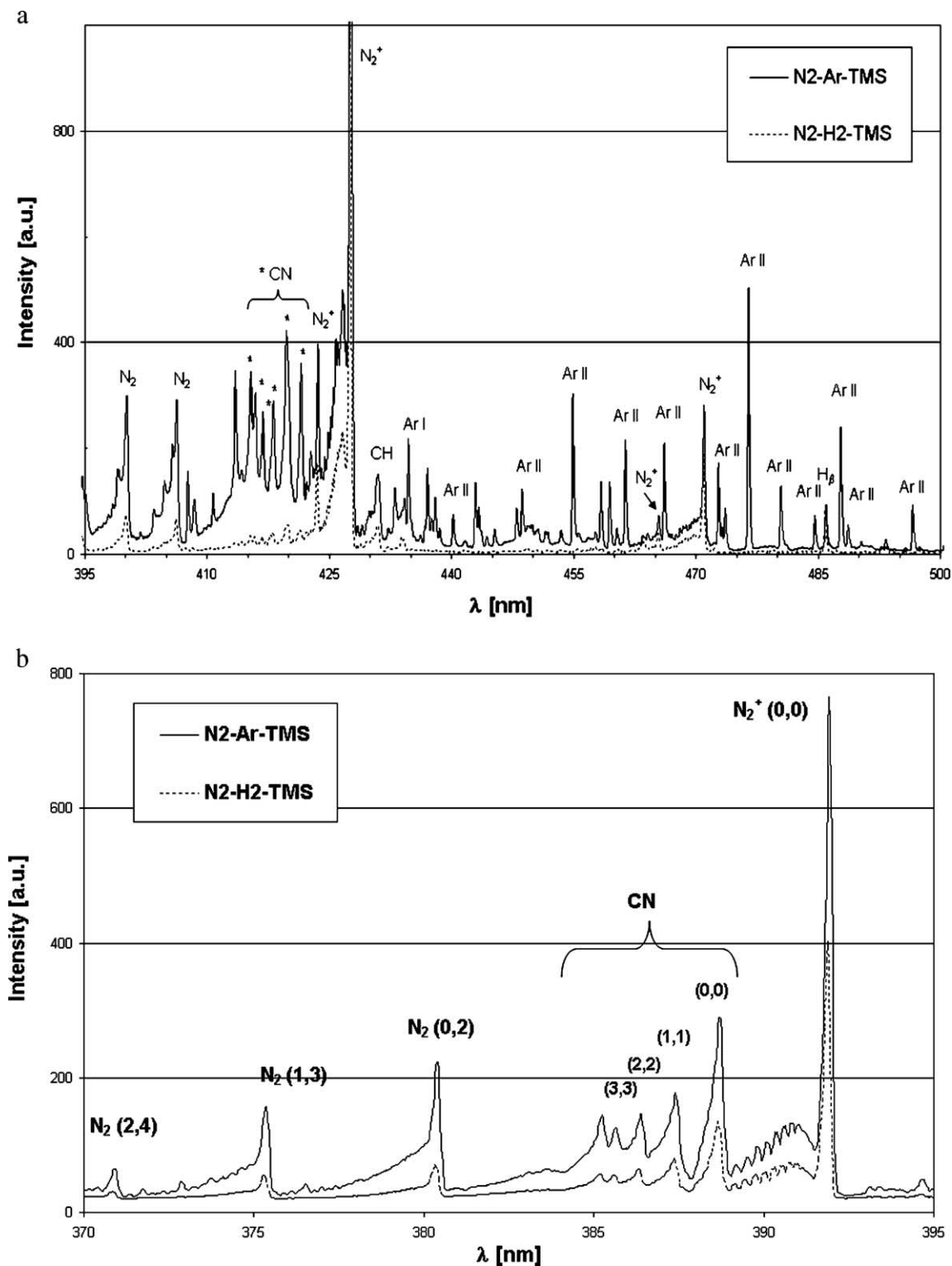

Fig. 2. (a, b) Spectra of the 100 kHz discharge in the N_2–Ar–TMS (N_2/Ar=1:1) (solid line) and N_2–H_2–TMS (N_2/H_2=1:1) (broken line) mixtures. (c) The low and high resolution spectra of Si I in the range of 200–290 nm (N_2–TMS mixture).
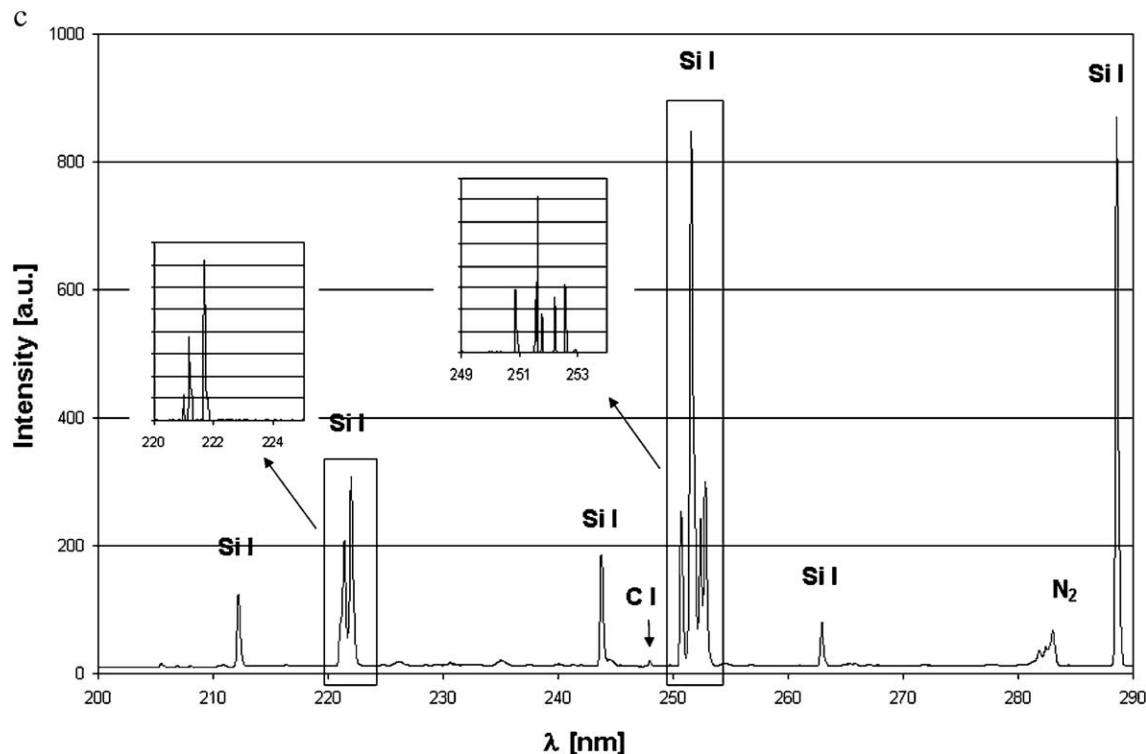
Fig. 2 (*continued*).

nation and destruction of vacuum pump by products of tetramethylsilane decomposition.

3. Results and discussion

The spectroscopy study of the tetramethylsilane decomposition process was carried out in the nitrogen–hydrogen and nitrogen–argon atmospheres.

3.1. Identification of active species in the $N_2-H_2-Si(CH_3)_4$ and $N_2-Ar-Si(CH_3)_4$ mixtures

The emission spectra were recorded in the wavelength range from 200 to 800 nm in order to identify active components, i.e. atoms or molecules in excited electronic, vibrational and rotational states, in the plasma phase. Typical emission spectra of nitrogen–hydrogen–tetramethylsilane and nitrogen–argon–tetramethylsilane mixtures are shown in Fig. 2a and b. The optical emission spectra were dominated by emission of bands of N_2^+ belonging to $B^2\Sigma_u^+-X^2\Sigma_g^+$ and bands of N_2 belonging to $C^3\Pi_u-B^3\Pi_g$ system. The weak spectra of N I (at 742.4; 744.2; 746.8; 818.8; 821.6 nm), N II (at 500.5; 500.1; 567.9 and 567.6 nm) and N_2 belonging to $(B^3\Pi_g-A^3\Sigma_u^+)$ transition were also observed in nitrogen rich plasmas. In the mixtures containing argon emission lines of Ar II and Ar I were excited. The most intense spectra of Ar II and Ar I were noticed in 450–520 and 650–780 nm regions, respectively. The hydrogen line Balmer series (H_α and H_β)

and NH ($A^3\Pi-X^3\Sigma^-$) with the band head at 336.0 nm was also detected in the examined mixtures. When tetramethylsilane was introduced into the discharge zone, in the 200–300 nm region, strong spectrum of silicon was observed (see Fig. 2c). Similar spectrum of Si I was identified in the mixture containing methyltrichlorosilane [16] and tetrachlorosilane [17]. The most intense Si I lines were at 251.6, 263.1 and 288.1 nm. In the plasma containing tetramethylsilane line of C I at 247.8 nm, the CH $A^2\Delta-X^2\Pi$ (0,0) at 431.4 nm and the weak spectrum of C_2 belonging to Swan system ($d^3\Pi_g-a^3\Pi_u$) with the band head at 516.5 (0,0) and at 512.9 nm (1,1) were noticed. The strong CN violet ($B^2\Sigma^+-X^2\Sigma^+$) (Fig. 2a and b) and weak red ($A^2\Pi-X^2\Sigma$) system were excited in the mixtures containing TMS and nitrogen. The appearance of SiN emission spectrum in the range of wavelength, 390–450 nm (the intense $A^2\Sigma-X^2\Sigma$ system) [19], was expected. However, the SiN spectrum has not been detected under experimental conditions applied here.

Only in the Ar–TMS discharge, emission band of SiH, the $A^2\Delta-X^2\Pi$ (0,0) transition with the Q-band head at 414.2 nm was additionally recorded. Similar spectrum of SiH was observed by Thomas and co-workers [20] in the same mixture, but in the microwave excited plasma.

3.2. Plasma temperature

The excitation, vibrational and rotational temperatures were measured for the N_2-H_2-TMS and $N_2-Ar-TMS$ mixtures at varying concentrations of nitrogen. Well-know
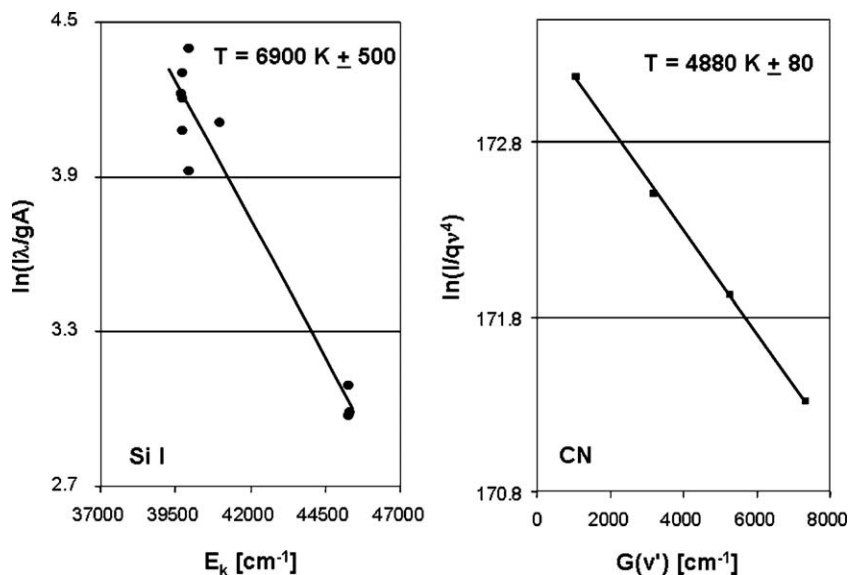
Fig. 3. The Boltzmann plots for Si I lines and CN bands.

equations (see, e.g. [1,21,23]) were used to determine the excitation, vibrational and rotational temperatures.

The electron "excitation" temperature (T_{exc}) of Ar I and Si I was measured from relative intensities of argon lines in the 640–755 nm region and silicon lines in the 220–290 nm region, assuming the Boltzmann distribution. Ten lines of Ar I (at 675.28; 687.13; 696.54; 703.03; 706.72; 714.70; 720.70; 727.29; 737.21; 751.47 nm) and 10 lines of Si I (at 220.80; 221.67; 221.80; 250.69; 251.43; 251.61; 251.92; 252.41; 252.85; 288.16 nm) have been chosen for measurement of T_{exc}. The Boltzmann plot for the Si I lines was presented in Fig. 3. The excitation temperature of H was calculated using two line radiation method [1], i.e. from ratio of emission intensity of the hydrogen lines: H_α (at 656.28 nm) and H_β (at 486.13 nm). The spectroscopic constants of Ar, Si and H, i.e. statistical weights, energies of the upper states and transition probabilities, were taken from Wiese and Martin table [22]. The relative standard deviation uncertainties for the excitation temperature of Si I and Ar I were up to 10–20%.

The Boltzmann plot method was also applied to calculate the vibrational temperatures (T_{vib}) of CN, N_2 and N_2^+. Theoretical background of the vibrational temperature measurements can be found elsewhere [1,4]. The vibrational temperature was determined from four bands of CN ($B^2\Sigma^+-X^2\Sigma^+$), i.e. (0,0), (1,1), (2,2) and (3,3), six bands of N_2, i.e. (0,2), (1,3), (2,4), (1,0), (2,1), (3,2), and two bands of N_2^+ ($B^2\Sigma_u^+-X^2\Sigma_g^+$), i.e. (0,1) and (1,2). The molecular constants and Franck–Condon factors of N_2, CN and N_2^+ were taken from Refs. [4,23]. The Boltzmann plot for CN was presented in Fig. 3. The estimated standard deviation uncertainties in the measurements of vibrational temperature were from 2% to 15%. The standard deviations (ΔT) for the CN vibrational temperatures (see Fig. 3 and Table 1) are very low due to the fact that bands belonging only to one sequence ($\Delta v = 0$) were measured. As a matter of fact the

temperature measurement uncertainties for CN are higher and are expected to be comparable with those for N_2.

In low pressure plasma the rotational temperature (T_{rot}) is assumed to be a good approximation of gas (kinetic) temperature [5]. The rotational temperature was determined from the N_2^+ spectrum by Boltzmann plot method. The N_2^+ (0,0) band of the ($B^2\Sigma_u^+-X^2\Sigma_g^+$) system with head at 391.44 nm was employed. The rotational structure of the (0,0) band of N_2^+ was recorded in fifth order by means of high resolution spectrograph. The rotational lines of the R-branch (from R4 to R21) of N_2^+ (0,0), practically free from spectral interferences and easy to be measured, were used.

The Ar I, Si I and H excitation temperatures are given in Table 1. The temperature of Si I increased clearly (from 4000 K to 9300 K) versus the fraction of nitrogen in the N_2-H_2-TMS gas feed. The temperature of H was almost constant (about 6000 K) when the nitrogen percentage varied from 0 to 75%. The maximum value of T_{exc}(H) was measured for the N_2–TMS mixture (7900 K). The Si I excitation temperature changes versus the nitrogen fraction found here for the N_2-H_2-TMS mixture are similar to those observed for the $SiCl_4-N_2-H_2$ and $SiCl_4-N_2-C_2H_2$ low pressure plasma [17]. Different higher temperature values of Ar I, Si I and H were obtained for N_2–Ar–TMS mixture (Table 1). The Ar I and Si I excitation temperatures varied from 9300 K to 10,700 K. Similar value of the excitation temperatures of Ar I and Si I implies that in the production of excitation state of silicon, the role of argon atoms is important. The excitation temperatures of Ar I and Si I were not sensitive to changes on the plasma gas composition. The excitation temperature of H was lower than the T_{exc}(Ar I) and T_{exc}(Si I) and varied in the range from 6200 K to 8200 K. Comparable values of T_{exc}(Ar I) and T_{exc}(H) were observed by Okada and Kijima [2] in the SiH_4-CH_4-Ar electrodeless inductively coupled discharge and by Jouberteau et al. [6] in the $Ar-N_2-H_2$ microwave plasma, respectively.

Table 1
The excitation (T_{exc}) and vibrational (T_{vib}) temperatures in the N_2–H_2–TMS and N_2–Ar–TMS mixtures

% N_2	N_2–H_2–TMS mixture					N_2–Ar–TMS mixture				
	0%	25%	50%	75%	100%	0%	25%	50%	75%	100%
T_{exc}(Ar I) [K]						9400±700	10560±1270	10640±1630	10650±2340	
T_{exc}(Si I) [K]	4000±420	6900±520	7980±920	8170±800	9300±1600	9200±2700	10600±2400	9920±2600	10700±1570	9300±1600
T_{exc}(H) [K]	5900	6270	6220	5900	7900	8200	6580	6520	6220	7900
T_{vib}(CN) [K]		5000±290	4880±80	4560±100	4280±130	6400±550	5700±30	5200±120	4900±200	4280±130
T_{vib}(N_2) [K]		2900±190	2920±180	3080±190	2500±310		2500±200	2480±220	2520±250	2500±310
T_{vib}(N_2^+) [K]		1470	1490	1540	1570		1530	1520	1500	1570

The CN, N_2 and N_2^+ vibrational temperatures for various N_2 percentages in the examined reactive mixtures are presented in Table 1. The highest value of vibrational temperature was observed for the CN molecule (4300–6400 K), while the T_{vib}(N_2) and T_{vib}(N_2^+) magnitudes were considerably lower, from 2500 K to 3100 K and from 1470 to 1570 K, respectively. However it should be considered that the vibrational temperature of N_2^+ was only evaluated from two bands. The growth of the N_2 fraction in the N_2–H_2–TMS and N_2–Ar–TMS mixtures led to fall of T_{vib}(CN) from 5000 K to 4300 K and from 6400 K to 4300 K, respectively. The observed difference between the vibrational temperatures of CN and N_2, i.e. T_{vib}(CN)> T_{vib}(N_2), may indicate that the excited CN and N_2 species are produced as a result of various excitation mechanisms. The electron impact excitation is probably the dominating process in case of vibrational excitation of the N_2 molecule. More complex processes based on impact of high energy species (hydrocarbon, carbon with active nitrogen) play a role in the case of excited states of CN. For the species examined here the vibrational temperatures measured in the N_2–H_2–TMS and N_2–Ar–TMS mixture were similar.

The N_2^+ rotational temperature in the nitrogen–hydrogen mixture increased from 530 K to 790 K with the growth of nitrogen fraction in the mixture (Fig. 4). The rotational temperature in argon–nitrogen mixture was practically independent on the gas composition and varied from 740 K to 790 K. Introduction of tetramethylsilane to the nitrogen–hydrogen or nitrogen–argon reactive mixtures resulted in lowering of the rotational temperature by about 100 K. It means that the $Si(CH_3)_4$ addition causes cooling of the gas temperature. The values of the rotational temperatures of N_2^+ obtained here for N_2–H_2 and N_2–Ar plasmas are in good agreement with the rotational temperature reported for other glow discharge [4].

The excitation, vibrational and rotational temperatures in examined mixtures were significantly different. The excitation temperatures are a few times higher than the rotational temperature and also higher than vibrational temperatures. Finally, the following relation between temperatures was observed in analyzed mixtures:

$$T_{exc}(\text{Ar I}) \approx T_{exc}(\text{Si I}) > T_{exc}(\text{H}) > T_{vib}(\text{CN}) > T_{vib}(N_2)$$
$$> T_{vib}(N_2^+) > T_{rot}(N_2^+)$$

The great differences between calculated temperatures indicated that plasma is far from equilibrium state.

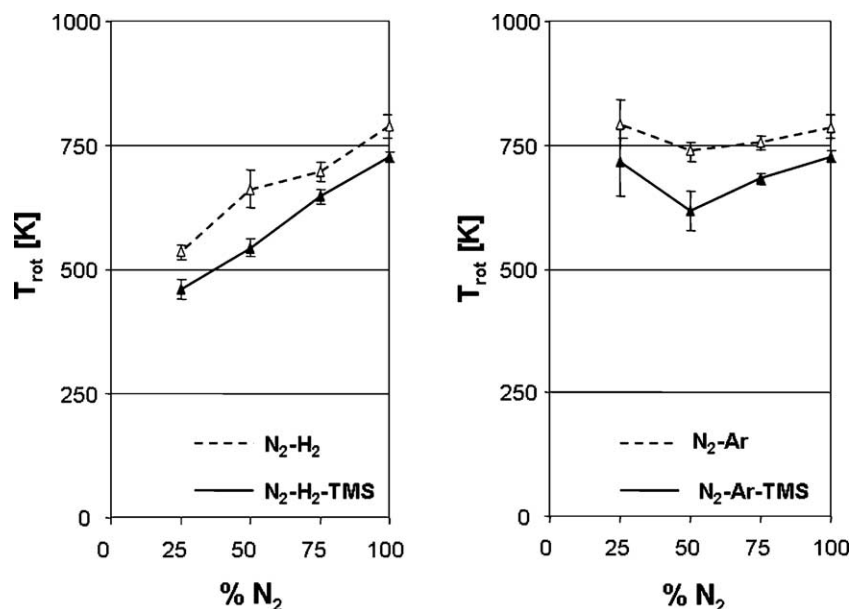Fig. 4. The rotational temperatures of N_2^+ in the N_2–H_2 and N_2–Ar mixtures with (solid line) and without (broken line) $Si(CH_3)_4$.
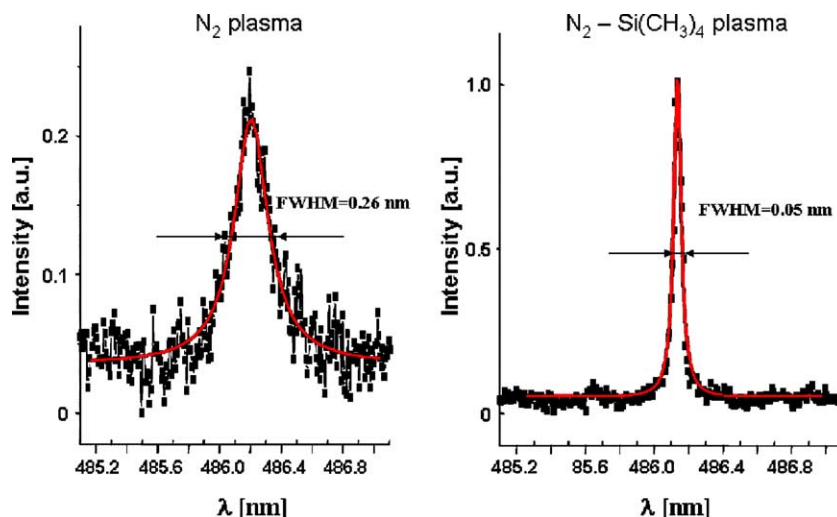
Fig. 5. The Lorentz profile and experimental measurements of the H_β line for the N_2 and N_2–$Si(CH_3)_4$ 100 kHz plasma.

3.3. Electron number density

The electron number density (N_e) was estimated from Stark broadening of H_β line (at 486.133 nm) using Griem formula [24]: $N_e = C(T_e, N_e) \times (\lambda_S)^{3/2}$, where λ_s is the Stark broadening of line in Å and $C(T_e, N_e) = 3.58 \times 10^{14}$ Å$^{-3/2}$ cm^{-3}—constant. The profile of hydrogen line was recorded in the second order by means of high resolution spectrograph with the dispersion of 130 pixels/nm. The experimental H_β line profile was fitted with the Lorentzian model (see Fig. 5). The Stark broadening deduced from experimental full width at half maximum (FWHM) was corrected for instrumental and Doppler full width (~ 0.03 nm). A standard deviation of N_e was determined to be up to 10%.

The electron number density is shown in Fig. 6 for the nitrogen–hydrogen and nitrogen–argon mixtures with and without addition of TMS. The electron density in the N_2–H_2 mixture increases with percentage of nitrogen, while in the N_2–Ar mixture the N_e remains practically constant. The observed increase of N_e in the N_2–H_2 mixture may result from the corresponding growth of nitrogen concentration, the main source of supplementary electrons. In the N_2–Ar mixture the secondary electrons are arisen from the ionization process of nitrogen and argon. The introduction tetramethylsilane to N_2–H_2 or N_2–Ar plasma caused a significant fall of electron number density. The observed decrease in electron number density should be due to the reduction of free electrons in plasma as a result of different reaction (e.g. cracking of bonds in the $Si(CH_3)_4$ molecule) and indicated an important role of

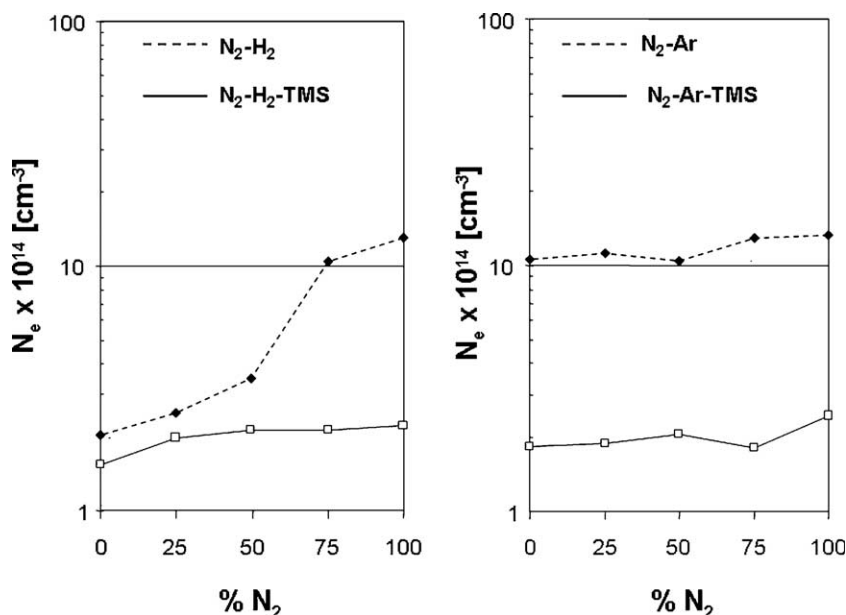Fig. 6. The electron number density in the N_2–H_2 and N_2–Ar plasma with (solid line) and without (broken line) tetramethylsilane.

Table 2
Spectroscopic data of the examined species

Species	λ [nm]	Transition	Threshold energy [eV]
Ar	750.39	$2p_1 - 1s_2$	13.48
Ar$^+$	487.20	$3p^4$ (^3P) $4p$ ($^2D^0$)$-3p^4$ (^3P) $4s$ (^2P)	19.68
C	247.80	$2p\,3s$ ($^1P^0$)$-2p^2$ (^1S)	7.68
H	656.28	$3d$ (^2D)$-2p$ ($^2P^0$)	12.08
Si	288.16	$3p\,4s$ ($^1P^o$)$-3p^2$ (^1D)	5.08
CH	431.40	$A^2\Delta - X^2\Pi$ (0,0)	2.9; $\sim 11^a$
N$_2$	380.49	$C^3\Pi_u - B^3\Pi_g$ (0,2)	11.2
N$_2^+$	391.44	$B^2\Sigma_u^+ - X^2\Sigma_g^+$ (0,0)	18.7
CN	388.43	$B^2\Sigma - X^2\Sigma$ (0,0)	3.2

[a] The threshold energy for CH considering various excitation processes.

electrons in the decomposition processes of TMS. The electron density found here is much higher than that measured in ECR-MW plasma [7] by Langmuir probe, but consistent with data obtained by optical emission methods for glow discharge [9].

3.4. Effect of nitrogen concentration on decomposition process of tetramethylsilane

Intensities of the following species, N$_2^+$, CN, N$_2$, Si, H, CH, C and additionally Ar, Ar$^+$, have been measured in order to investigate the Si(CH$_3$)$_4$ decomposition process in the reactive mixtures. These species may also play an important role in the production and growth of the SiCN layers. Spectral lines and molecular bands employed for the intensity measurements were presented in Table 2. The emission intensities of lines and bands of species were monitored versus percentage of nitrogen in the nitrogen–hydrogen–TMS and nitrogen–argon–TMS mixtures.

In the N$_2$–H$_2$–TMS plasma (Fig. 7), the emission intensities of N$_2^+$, CH and Si increased with the growth of nitrogen fraction in gas feed. These results are consistent with the increase of electron density versus the growth of nitrogen percentage (see Fig. 5a). For N$_2$, CN and C the relation between emission intensity and the nitrogen percentage was similar and a maximum intensity at 75% of N$_2$ was observed.

In the N$_2$–Ar–TMS mixture (Fig. 8) the emission intensities of N$_2^+$ and Ar were proportional to the fraction of nitrogen and argon in the gas mixture, respectively. The CN and N$_2$ intensities increased versus % N$_2$ up to a maximum at 75% N$_2$ as it was observed also for the N$_2$–H$_2$–TMS mixture. The emission intensities of Ar$^+$, H, CH and C decreased with increasing nitrogen content in the mixture, but the intensity decrease was not very significant for H, CH and C species. The intensity of Si reached minimum at N$_2$/Ar=1:1. The Si I intensity for Ar–TMS mixture was higher than recorded for the N$_2$–TMS mixture.

The experimental results for Si, C, H and CH species (see Fig. 8) suggest that argon atoms, probably in metastable states, contribute in the cracking process of TMS. Jauberteau and co-workers [25] investigated the Ar–Si(CH$_3$)$_4$ plasma and reported that the role of metastable form of argon was very important for breaking of Si–C bonds in the Si(CH$_3$)$_4$ molecule.

A variety of reactions can potentially occur during introduction of Si(CH$_3$)$_4$ to reactive mixture. In the N$_2$–H$_2$–TMS and N$_2$–Ar–TMS mixtures electron impact dissociation is the main channel for decomposition of TMS as it can be concluded from the electron density measurements (see Fig. 6). The breaking of the Si–CH$_3$ bonds is probably the first fragmentation step of TMS in
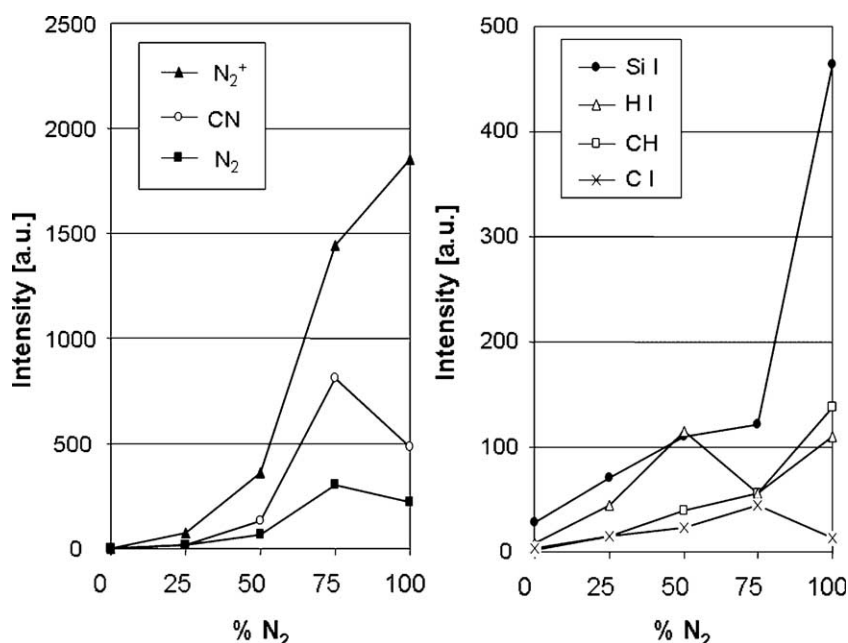
Fig. 7. The variation of the N$_2^+$, CN, N$_2$, Si, H, CH and C intensities versus the nitrogen percentage in the N$_2$–H$_2$–TMS mixture.
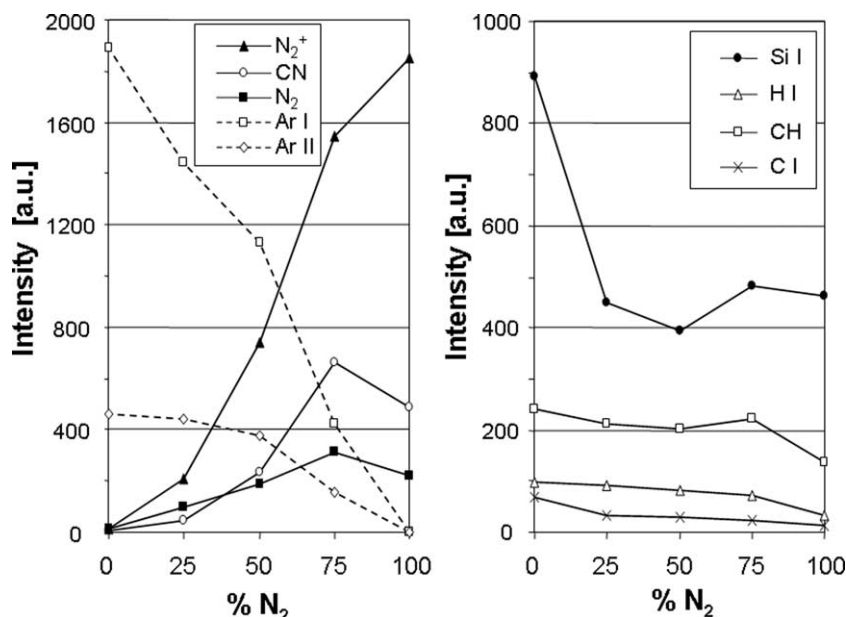
Fig. 8. The N_2^+, CN, N_2, Ar, Ar^+, Si, H, CH and C emission intensities as a function of nitrogen fraction in the N_2–Ar–TMS mixture.

plasma, because the energy of the Si–C bond is lower than the energy of the C–H bond.

In order to better understand the gas phase chemistry in the N_2–H_2–TMS mixture optical actinometry technique, developed by Coburn and Chen [26] and d'Agostino [27], was also applied. Actinometry is based on the addition of inert gas, so-called actinometer, to discharge zone and on the monitoring of the emission intensities coming from actinometer and analyzed species. This method enables to determine the relative concentrations of species in their ground state, if the threshold energy of actinometer is close to the threshold of the analyzed species. The actinometry technique so far was validated only for H atoms [28], but it

Fig. 9. The actinometric relative concentrations of species versus fraction of nitrogen in the N_2–H_2–TMS mixture.

was also often used for the following species: CH, CN, C [4,27].

A small and constant quantity of argon ($\sim 4\%$) (actinometer) was added to the N_2–H_2–TMS reactive mixture and the emission intensity of Ar I line at 750.4 nm was measured versus the nitrogen concentration. The N_2, H, CN and C relative concentrations can be expressed by the ratio of the N_2, H, CN and C emission intensities to emission of Ar I line, respectively. Similar procedure was also used here to investigate the CH relative concentrations versus nitrogen percentage. The excitation energies of N_2 (11 eV) and H (12 eV) and threshold energy of the production of CH (~ 11 eV) are close to the excitation energy of argon (13.5 eV), whereas the CN and C species and Ar have different excitation energies (see Table 2). Nevertheless, on the basis of the earlier works [4,27], the optical actinometry technique was employed here to determine the CN and C concentrations. Fig. 9 illustrates the emission intensities of CN, N_2, H, CH and C normalized to intensity of Ar I line as a function of nitrogen percentage in the N_2–H_2–Si($CH_3)_4$ mixture. The concentrations of the following species, C, CN and N_2, increase with the growth of nitrogen percentage and reach a maximum at 75% of N_2. Similar behavior of concentrations of investigated species versus % N_2 may suggest that the CN radicals are formed as a result of reaction between carbon (or hydrocarbon) and nitrogen. The actinometric concentrations of H atoms decrease linearly with the growth percentage of nitrogen, while the I(CH)/I(Ar) increase.
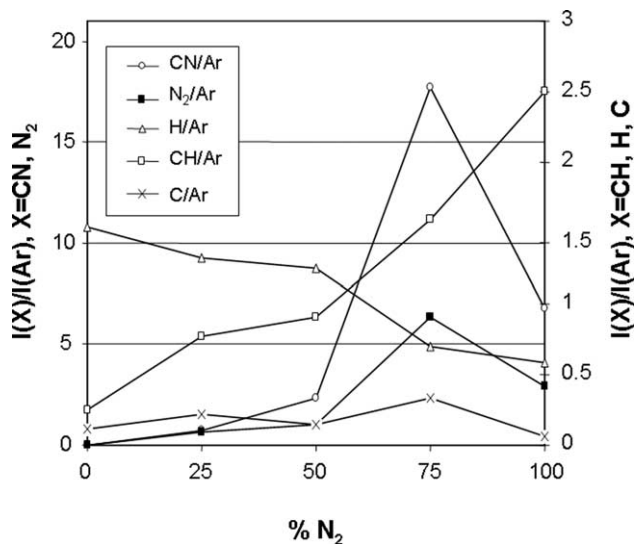
4. Conclusion

Optical emission spectroscopy (OES) was found to be useful for investigation of the decomposition process of

tetramethylsilane in the nitrogen–hydrogen and nitrogen–argon mixtures. For the first time, for the N_2–H_2 and N_2–Ar reactive mixture with addition of organosilicon compound, the fundamental plasma parameters, i.e. the excitation, vibrational and rotational temperatures and electron number density, were determined. The difference in the temperatures $(T_{exc} > T_{vib} > T_{rot})$ has indicated a strong deviation from plasma equilibrium state. The introduction of $Si(CH_3)_4$ to N_2–H_2 or N_2–Ar reactive mixtures caused the fall of rotational temperature and electron number density. The temperatures and electron number density in the N_2–H_2–TMS mixture were significantly dependent on nitrogen percentage, while the contribution of nitrogen in the N_2–Ar–TMS mixture did not affect the plasma parameters.

The optical actinometry technique was found to be useful to evaluate the ground state concentrations of the plasma components.

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