Study of the acetylene–nitrogen, hydrogen–nitrogen and nitrogen with the addition of silicon tetrachloride, 100 kHz low pressure discharge by optical emission spectroscopy

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The 100 kHz low pressure discharge in different reactive gases, i.e. acetylene – nitrogen, hydrogen – nitrogen and nitrogen, with addition silicon tetrachloride, has been studied here by means of optical emission spectroscopy. Optical emission was used to identify active plasma components: i.e. excited atoms, ions, radicals and molecules. Emission intensities of main species were monitored versus various experimental parameters, among them kind of reactive gases. The discharges were characterized by N_2^+ rotational temperature, N_2 vibrational temperature and Si I excitation temperature. The influence of the reactive gases on a decomposition process of silicon tetrachloride was investigated. Plasma processes and plasma equilibrium state were discussed.

1 Introduction

Reactions occurring in the systems containing silicon tetrachloride are of a great interest because these compound are widely used for the synthesis and deposition of different materials and thin layers of Si [1], SiN [2], SiO_2 [3] and for reactive plasma etching of materials [4]. Especially, reaction in the mixtures containing silicon tetrachloride with nitrogen, nitrogen – hydrogen and nitrogen – acetylene are important, because these mixtures may be alternative for plasma enhanced production of a–SiN and a–SiCN materials. In order to understand mechanism leading to the formation of the materials it is necessary to investigate plasma parameters and phenomena occurring in plasma phase. Optical temperatures (excitation, vibrational, rotational and kinetic) are very important parameters for understanding and description of various plasma processes, investigation of plasma non–equilibrium state and energy distributions. Optical emission spectroscopy (OES) is noninvasive, in situ and simple technique which enables to study chemical and physical processes in the plasma and determination of temperatures. Recently, the OES has been used for investigation of system containing silicon and halogen [5], [6], [7], for deposition of silicon [1], [8] and reactive etching of materials [4]. However, the OES gives only an information about excited species but not directly of the species in their ground

state. The technique that can be utilized for measurements of relative concentration of species in the ground state, used formerly for investigation of silicon plasma [7], [9] is optical actinometry [10].

In this work the optical emission spectroscopy and optical actinometry technique based on OES were used to study decomposition of silicon tetrachloride in the nitrogen – hydrogen, nitrogen – acetylene and in pure nitrogen 100 kHz plasmas. Plasma parameters, i.e. the Si excitation temperature, N_2 vibrational temperature and N_2^+ rotational temperature were determined and compared. On the base the plasma species concentration measurements, several chemical reactions were proposed and discussed. The plasma equilibrium state was analysed.

2 Experimental

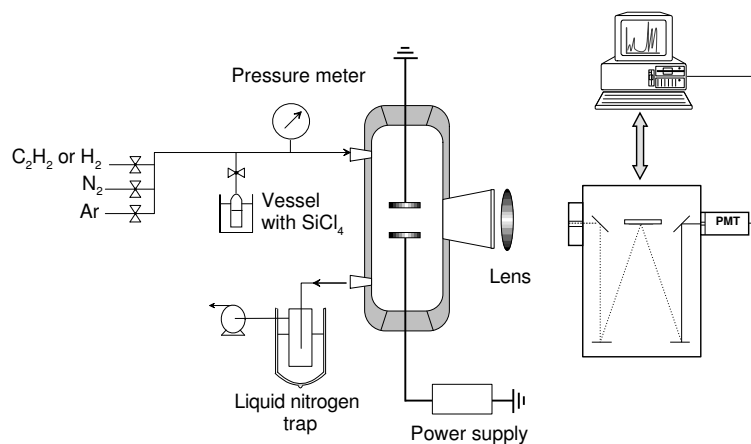The experimental set–up is schematically shown in Fig. 1.

Fig. 1. The experimental setup.

The discharge was generated in cylindrical Pyrex glass chamber including two parallel steel electrodes (diameter 22 mm, thickness 2 mm, space between the electrodes 16 mm) connected to 100 kHz power supply (maximum power 200 W). The vessel with silicon tetrachloride, $SiCl_4$ (Merck, 99% grade, bp. 58°C) was held at a constant temperature of 0°C in a water – ice bath. The silicon tetrachloride was introduced by means of Teflon valve in the stream of gases introduced into the chamber. The total pressure was measured using thermocouple gauge. The nitrogen – hydrogen and nitrogen – acetylene mixtures (containing 25, 50 and 75% of nitrogen) and pure nitrogen were employed here as reactive gases. The current of discharge, total pressure and flow rate of silicon tetrachloride were kept constant and equaled to: 100 mA, 532 Pa (4 Tr) and 0.04 g min^{-1}, respectively. Additionally, a small and constant quantity of argon ($\approx 4\%$) was added to the reactive mixture for the optical actinometry measurements. A JY Triax 320 monochromator (grating 1200 grooves mm^{-1}) with Hamamatsu R–928 photomultiplier was used for mea-

surements of emission intensities in the 200 – 850 nm region. The high–resolution emission spectra were measured by means of Carl Zeiss Jena PGS–2 spectrograph with Hamamatsu DH–3 photomultiplier connected to the computer. Emission intensity was measured near the powered electrode (2 mm above the substrate surface i.e. cathode glow region). The optical system was calibrated using reference standard lamp (Bentham).

3 Results and discussion

3.1 Emission spectra

In the reactive mixtures containing nitrogen, bands of the N_2 $C^3\Pi_u$–$B^3\Pi_g$, $B^3\Pi_g$–$A^3\Sigma_u^+$ and N_2^+ $B^2\Sigma_u^+$–$X^2\Sigma_g^+$ systems and lines of N I (at 742.4; 744.2; 746.8 nm) were observed. In the nitrogen–silicon tetrachloride mixture: Si I lines (the most intensive at 288.3; 251.4 and 243.5 nm), very weak Si II lines (at 634.7 nm and 637.2 nm), continuum in the range 525 – 620 nm with the maximum at 555 nm (probably due to $SiCl_2$ a^3B_1–X^1A_1) molecule emission [11]), bands of SiCl $B^{'2}\Delta$–$X^2\Pi_r$ (at 286.6 and 280.97 nm), weak Cl I lines (at 754.7 and 837.6 nm) and very weak Cl II lines (at 478.1 and 490.5 nm) were identified. Introduction of hydrogen to N_2–$SiCl_4$ plasma resulted in emission spectra of Hα (at 656.28 nm), H$_\beta$ (at 486.13 nm) and Hγ (at 434.4 nm) and NH (the $A^3\Pi$ – $X^3\Sigma^-$ band at 336.0 nm, partially overlapped by very intense band of N_2 (0–0), with head at 337.1 nm). Emission spectra of species coming from $SiCl_4$ i.e. Si, SiCl, $SiCl_2$ and Cl were also observed. In the N_2–C_2H_2–$SiCl_4$ plasma in addition to very intense bands of N_2, N_2^+, lines of Si, weak lines of Cl and bands of SiCl, $SiCl_2$, a several products of acetylene dissociation: CH (the 431,4 nm band of the $A^2\Delta$–$X^2\Pi$ system), hydrogen (Hα and H$_\beta$ lines) and carbon (C I at 247.8 nm) were identified. The cyanide radical (CN) bands of the violet system ($B^2\Sigma^+$–$X^2\Sigma^+$) and very weak bands of the red system ($A^2\Pi$–$X^2\Sigma$) were also noticed. The CN molecules originate as a result of reaction of acetylene, or other hydrocarbon species in plasma, with active nitrogen. Emission spectra of SiN and SiH have not been detected under experimental conditions of this study.

3.2 Optical emission spectroscopy and actinometry

Table 1 lists main spectroscopic constants of examined species, such as wavelengths of lines and bands measured, transitions and respective excitation energies. Changes of emission intensity of actinometer (Ar I at 750.3 nm) and emission intensities of N_2, CN and N_2^+ species as a function plasma gas composition are presented in the Fig. 2.

Increase of the nitrogen concentration in the gas mixture led to growth of the emission intensities of N_2, Ar in the N_2–H_2–$SiCl_4$ and N_2, Ar, CN in the N_2–C_2H_2–$SiCl_4$ mixture. In the N_2–$SiCl_4$ mixture the emission spectra of CN were not detected. For the nitrogen – hydrogen mixture a maximum in intensity of N_2^+ for 75% of nitrogen was observed, whereas in the nitrogen – acetylene mixture the

Table 1
Spectroscopic data of species

Species	Wavelength [nm]	Transition	Excitation energy [eV]
Si	288.16	$3p4s\ ^1P_0 - 3p^2\ ^1D$	5.1
Cl	837.59	$3p^44p\ ^4D_0 - 3p^44s\ ^4P$	10.4
H_β	486.13	$4d^2\ D^0_{3/2} - 2p^2\ P^0_{1/2}$	12.1
CH	431.4	$A^2\Delta - X^2\Pi\ (0\text{-}0)$	2.9[a]
CN	388.43	$B^2\Sigma - X^2\Sigma\ (0\text{-}0)$	3.2[a]
N_2	380.49	$C^3\Pi_u - B^3\Pi_g\ (0\text{-}2)$	11.2[a]
N_2^+	391.44	$B^2\Sigma^+_u - X^2\Sigma^+_g\ (0\text{-}0)$	3.1[a]; 18.7[b]
Ar	750.39	$2p_1 - 1s_2$ [c]	13.5

[a] Energy of the upper electronic state
[b] Total energy of electronic- vibrational excitation from the ground state of N_2
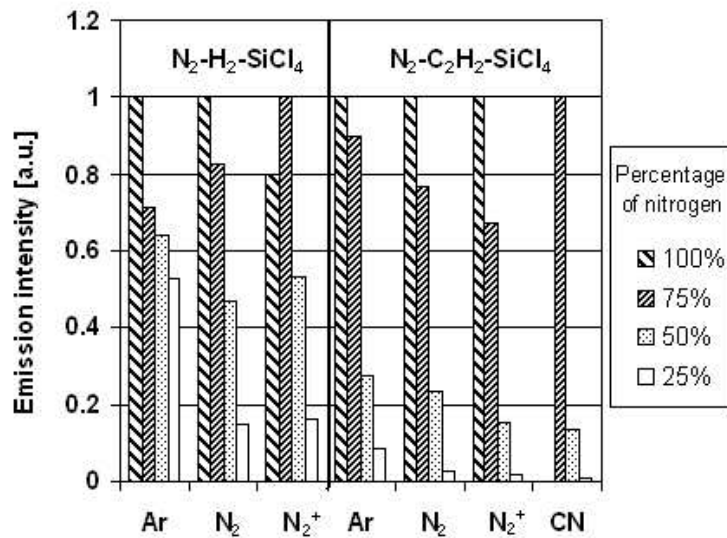[c] Paschen notation

Fig. 2. Emission intensities of Ar, N_2, CN and N_2^+ species for various nitrogen contents in the $SiCl_4$–N_2–H_2 and $SiCl_4$–N_2–C_2H_2 mixture.

emission intensity of N_2^+ increase with concentration of nitrogen in the plasma. The Ar I (750.4 nm line, $2p_1$-$1s_2$ transition) is mainly excited by direct electron impact from the ground state [10] and the emission intensity of argon (I_{Ar}) is proportional to density of Ar in the ground state (n_{Ar}), electron density (n_e) and coefficient of

the excitation rate (C_{exc}):

$$I_{Ar} \; = \; k C_{exc} \; n_e \; n_{Ar} \tag{1}$$

The coefficient C_{exc} depends on the electron energy distribution function and cross - section for electron collision. According to equation (1) the change of actinometer intensity has been assumed to represent plasma activity trends [9] i.e. change in the electron number density or in the mean electron energy (or both). The growth of emission intensity of argon with concentration of nitrogen indicated that the electron number density and/or mean electron energy increased with content nitrogen both in the acetylene – nitrogen – silicon tetrachloride and hydrogen – nitrogen – silicon tetrachloride mixtures.

The emission intensities of H, Si, Cl and CH (only for acetylene – nitrogen mixture) normalized to argon intensity have been chosen to monitor the behavior of concentrations of species versus the content of nitrogen in the N_2–H_2–$SiCl_4$ and N_2–C_2H_2–$SiCl_4$ mixtures (Fig. 3).
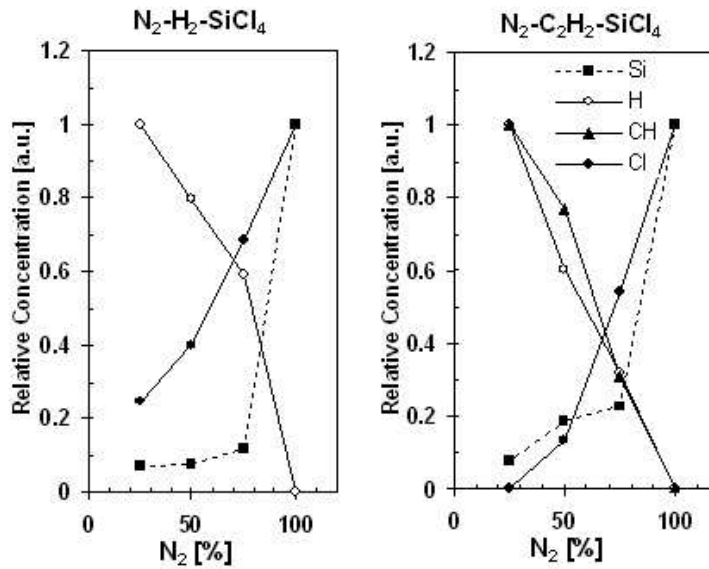

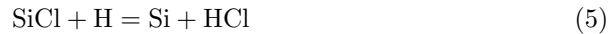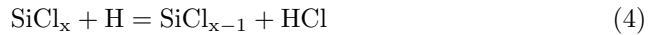Fig. 3. The changes of H, CH, Si and Cl concentration in the plasma versus gas composition.

In the both mixtures, the concentration of the silicon increased with content of nitrogen. The maximum of Si concentration was noticed for N_2–$SiCl_4$ discharge. The introduction of acetylene or hydrogen caused a significant fall of silicon concentration. The change of nitrogen concentration from 75 % to 25 % in hydrogen – nitrogen and acetylene – nitrogen mixture led to slight decrease of silicon concentration. The concentrations of Cl increased with content of nitrogen in mixtures, while

the drop of concentration of hydrogen (both in acetylene – nitrogen and hydrogen – nitrogen mixtures) and CH (in nitrogen – acetylene mixture) were observed.

The $SiCl_4$ or other fragments coming from silicon tetrachloride (e.g. Si_xCl_y, $SiCl_y$) may be dissociated [1] by electron – molecule mechanism:

$$SiCl_x + e = SiCl_{x-1} + Cl + e \tag{2}$$

$$SiCl + e = Si + Cl + e \tag{3}$$
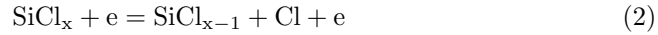
and neutral – neutral mechanism:

$$SiCl_x + H = SiCl_{x-1} + HCl \tag{4}$$

$$SiCl + H = Si + HCl \tag{5}$$

In the N_2–$SiCl_4$ mixture the main mechanism leading to the formation of Si atoms is reaction (3) i.e. the electron – molecule reaction. For N_2–H_2–$SiCl_4$ and N_2–C_2H_2–$SiCl_4$ mixtures the two mechanism leading to the formation of Si i.e. electron – molecule and neutral – neutral seem to play an important role. In the acetylene – nitrogen plasma with addition of $SiCl_4$ among different reactions leading to production of the CH and H species in plasma, dissociation of acetylene by electron impact seems to be the most significant:

$$C_2H_2 + e = 2CH + e \tag{6}$$

$$C_2H_2 + e = C_2H + H + e \tag{7}$$

In the hydrogen – nitrogen plasma (cathode glow region) the H radical may originate from the reaction [10]:

$$N_2^+ + H_2 = N_2H^+ + H \tag{8}$$

In the mixtures: N_2–H_2–$SiCl_4$, N_2–C_2H_2–$SiCl_4$ and N_2–$SiCl_4$ various neutral and ion polyatomic species may be formed as a results ion – molecule and/or polymerization processes. These species are impossible to identified by OES methods.

3.3 Optical temperature

The temperature is an important parameter characterizing plasma. Temperature influences physical and chemical processes. The temperature determination from different species permits the characterization of non – equilibrium state of plasma. Assuming the partial local thermal equilibrium state the excitation, vibrational and rotational temperatures were determined from the Boltzman plots [12]. For measurement of the excitation temperature ten lines of Si I (i.e. 220.80; 221.67; 221.80; 250.69; 251.43; 251.61; 251.92; 252.41; 252.85 and 288.16 nm) with the upper state energies from 4.9 to 6.2 eV were used. The vibrational temperature of

N_2 was calculated using (3–2) (2–1) (1–0) (2–4) (1–3) (0–2) bands of the $C^3\Pi_u$–$B^3\Pi_g$ system. The rotational temperature was determined on the base of R–lines of the N_2^+ $B^2\Sigma_u^+$–$X^2\Sigma_g^+$ (0–0) transition. In the Fig. 4 the rotational, vibrational and excitation temperatures for the N_2–$SiCl_4$, N_2–H_2–$SiCl_4$ (N_2:H_2=1:1) and N_2 –C_2H_2–$SiCl_4$ (N_2:C_2H_2=1:1) mixtures are given. The rotational (N_2^+), excitation (Si I) and vibrational (N_2) temperatures were found to related be to the plasma gas composition. The highest values of the excitation and rotational temperatures were observed in the N_2–$SiCl_4$ discharge. The introduction acetylene or hydrogen to the N_2–$SiCl_4$ mixture caused a decrease of excitation and rotational temperatures as can been seen in the Fig. 4.
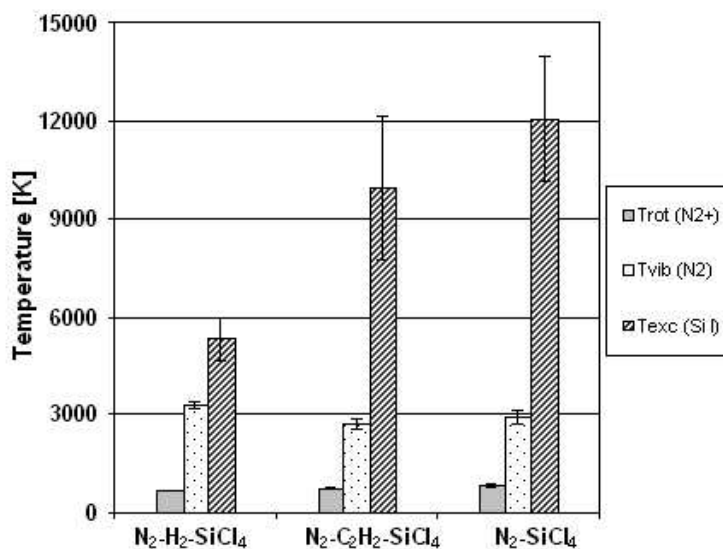

Fig. 4. The excitation temperature of Si I, vibrational temperature of N_2 and rotational temperature of N_2^+ in the $SiCl_4$–N_2–H_2 (N_2/H_2=1/1), $SiCl_4$–N_2–C_2H_2 (N_2/C_2H_2=1/1) and $SiCl_4$–N_2 mixtures.

For the excitation temperature the lowering was very significant. The vibrational temperature of N_2 varied rather imperceptibly (2700 K – 3250 K) and was the highest for N_2–H_2–$SiCl_4$ (N_2:H_2=1:1) mixture. The great differences between the excitation, rotational and vibrational temperatures indicate that the N_2–$SiCl_4$, N_2–H_2–$SiCl_4$ (N_2:H_2=1:1) and N_2–C_2H_2–$SiCl_4$ (N_2:C_2H_2=1:1) 100 kHz plasma were not in equilibrium state.

4 Conclusions

To conclude, we have shown that optical emission spectroscopy and based on OES optical actinometry technique are very suitable for investigation the 100 kHz discharges in the nitrogen, nitrogen – hydrogen and acetylene – nitrogen mixture with addition of silicon tetrachloride. The concentrations of active plasma species were found to be strongly dependent on the contents of nitrogen in the N_2–H_2–$SiCl_4$ and N_2–C_2H_2–$SiCl_4$ mixtures. The optical temperatures have been related to the plasma gas composition. The N_2^+ rotational temperature and Si I excitation temperature were very sensitive for changes of the plasma gas composition and varied from 660 K to 830 K and from 5300 K to 12000 K, respectively. The trends of changes of excitation and rotational temperatures were similar for investigated mixtures. The vibrational temperature of N_2 was slightly related to the mixture composition. The plasma generated in the N_2–$SiCl_4$, N_2–H_2–$SiCl_4$ and N_2–C_2H_2–$SiCl_4$ mixture by means of the 100 kHz discharge is far from equilibrium state.

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