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STUDY OF PLASMA PROCESSES IN AFTERGLOW BY MEANS OF ELECTRON SPIN RESONANCE [1]

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This contribution is intended to summarize in a practically useful form the basic information about the detection of the gas phase atoms and free radicals by electron spin resonance spectroscopy (ESR) in gas discharge afterglow and in remote plasma reactors. This paper shows how ESR could be effectively used for the monitoring of relative or absolute concentrations of gas phase H, O, N atoms during the volume plasma chemical and wall recombination processes.

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1 Introduction

Electron spin/paramagnetic resonance effect is based on resonant absorption of microwave photons by transitions between Zeeman split energy levels. Before entering into discussion of the spectra of the individual species taking part in plasma chemical processes, there are certain remarks, which apply generally that ought to be noted. Nearly all of the transitions of interest involve the absorption of magnetic dipole radiation between Zeeman levels. All of the transitions of interest for present purposes will be governed by the selection rule on the magnetic quantum number $\Delta M_J = \pm 1$, so that for absorption of either electric or magnetic dipole radiation a component of the corresponding field vector must be perpendicular to the external magnetic field. With the addition of a nuclear spin I in the strong field limit, J and I are uncoupled from each other and interact separately with the field. Since there are $2J+1$ values of M_J and $2I+1$ values for $M_I(\Delta M = 0)$ the total number of spectral lines for given J and I is $2J(2I+1)$. Summary of some atoms and species whose gas phase ESR spectra have been detected experimentally is presented e.g. in [1].

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2 Determination of rate coefficients of gas phase chemical reaction by ESR

The processes for the deposition of SiC, SiO_2 and Si_3N_4-like films by plasma – enhanced chemical vapor deposition (PECVD) in radiofrequency or microwave plasma reactors are generally used for synthesis of amorphous materials. Kinetics of the reactions H+SiH_4, O+TEOS (tetraethoxysilane) and N+HMDSZ (hexamethyldisilazane) were studied in works [2-4].

In the present study the ESR flow tube technique has been applied to characterize the reactant combinations that are of interest in the synthesis of amorphous SiO_2 and Si_3N_4–like materials. Study of reaction kinetics by ESR was described in detail in [1, 5]. Gas phase chemical reactions for deposition of a-Si:H, a-Si:CH, SiO_2-like and Si_3N_4-like materials in a remote hydrogen and oxygen plasma reactor have been quantitatively characterized with ESR in [2-7]. A schematic drawing of the experimental setup is presented in Fig. 1. The plasma discharge was sustained in the quartz tube within a cavity (13.56 MHz, 25 W). Pure molecular N_2 (O_2) was injected into the plasma through a quartz tube that passed, after a right-angle bend, into the ESR cavity (X-band). The density of [N] or [O] atoms in the distance 35 cm from the plasma exciting RF cavity reaches more than 10^{14} cm^{-3}. Between the two cavities the HMDSZ or TEOS vapors were injected into the flux of partially atomized N_2 or O_2 via small diameter tube. The total pressure in the ESR cavity cavity during all measurements was maintained at 250 Pa. The ESR spectrometer was calibrated with molecular oxygen as is described in [1]. ESR measurements provided absolute values of [N] or [O] and the correction for the loss of [N] ([O]) by processes that are first order in N (O) and independent of HMDSZ (TEOS), such as wall recombination.

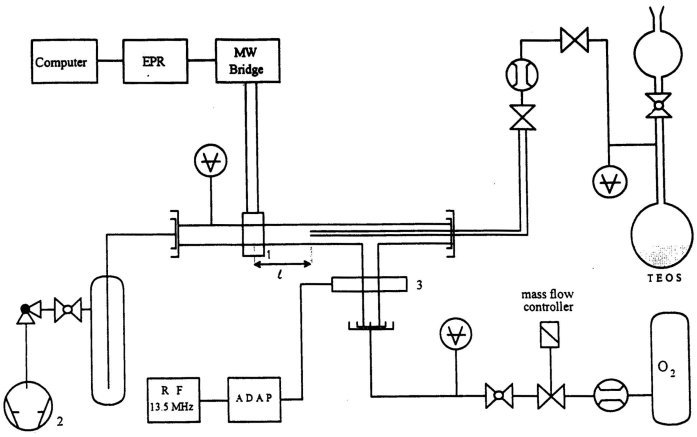

Fig. 1. Apparatus used for determination of O+TEOS and N+HMDSZ kinetics. 1 - ESR cavity, 2 - pumping system, 3 - RF discharge cavity.

Monitoring of N-atom (O-atom) loss as a function of time (residential time) was the basis of this experiment. Correction for the [N] or [O] loss due to the wall recombination is achieved by recording [N] or [O] at each position x downstream from the injector both with ("on") and without ("off") flowing HMDSZ (TEOS). For the case without flowing HMDSZ we can write

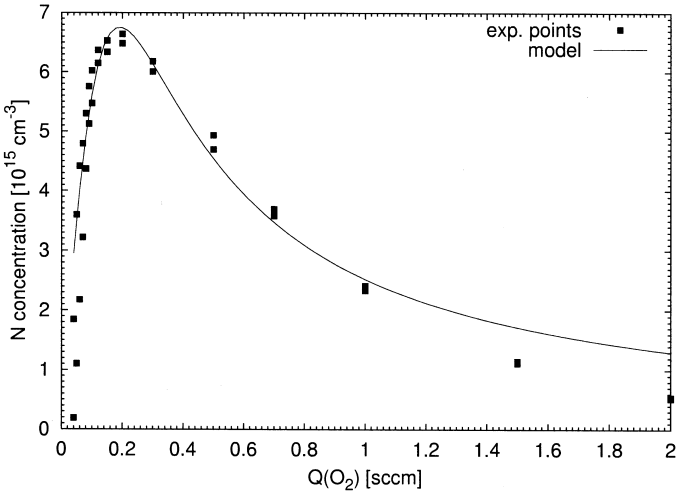

Fig. 2. Nitrogen atom density in afterglow as a function of O_2 admixture concentration. Experiment was carried out at 450 Pa, nitrogen flow was 50 sccm. (1 sccm=1.7×10^{-3} Pa m^{3}s^{-1}).

for the the N-atom density

$$\mathrm{d}[N]_{\mathrm{off}}/\mathrm{d}t = -k_2[N]_{\mathrm{off}} \Rightarrow [N]_{\mathrm{off}}[N_2]_0/[N_2]_{\mathrm{x}} = C_1 \exp(-k_2 t), \tag{1}$$

where k_2 is the wall recombination coefficient, C_1 is a constant depending on experimental arrangement, x is the distance of ESR cavity from plasma exciting RF discharge. From (1) we get for the case with flowing HMDSZ

$$\begin{aligned} \mathrm{d}[N]_{\mathrm{on}}/\mathrm{d}t &= -(k_2 + k_1 \cdot C_{\mathrm{HMDSZ}}) \cdot [N]_{\mathrm{on}} \\ &\Downarrow \\ [N]_{\mathrm{on}} \cdot [N_2]_0/[N_2]_{\mathrm{x}} &= C_2 \cdot \exp[-(k_2 + k_1 \cdot C_{\mathrm{HMDSZ}})t], \end{aligned} \tag{2}$$

where $k_1$is the rate coefficient of the reaction N+HMDSZ, C_2 is const. given by experimental conditions and C_{HMDSZ} is the HMDSZ concentration.

By dividing (2) and (1) and taking logarithm of both sides we obtain

$$\ln([N]_{\mathrm{on}}/[N]_{\mathrm{off}}) = C_0 - k_1 \cdot C_{\mathrm{HMDSZ}} \cdot t. \tag{3}$$

The rate constant k_1 can be determined from the linear dependence (3).

For the reaction O+TEOS, the rate coefficient k_1 ranges from 7.1 to 9.2 $[10^{-15}$ cm^{3}s$^{-1}]$ and for reaction N+HMDSZ was found k_2 = (0.75 – 2.4)·10^{-15} [cm^{3}s^{-1}].

3 The effect of admixtures and wall recombination of atoms

The dependencies of the dissociation rates of oxygen, hydrogen and nitrogen on the admixture concentration were examined by ESR. In all experimental dependencies we can see the rapid

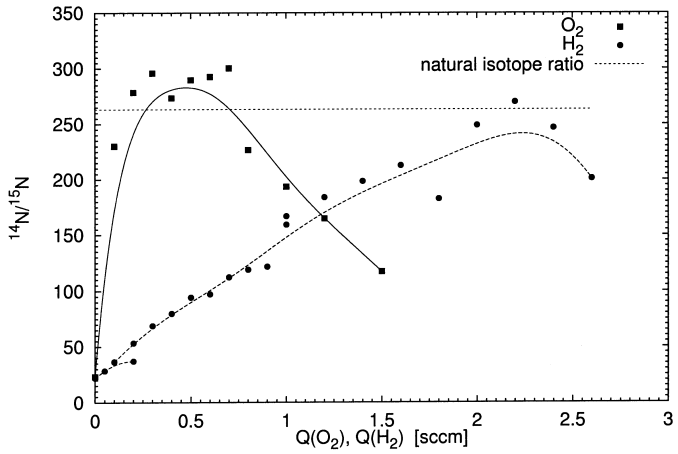

Fig. 3. Ratio of nitrogen isotope abundance in afterglow as a function of the amount of O_2 or H_2 admixturer. Flow of nitrogen was 50 sccm, corresponding to a pressure 450 Pa.

dissociation rate increase with the growing amount of admixture and after the maximum has been reached, the next increase of the amount of admixture leads to an atom concentration decrease as shown in Fig. 2. But the steepness of the increase and decrease as well as the position of the concentration maximum with respect to the admixture concentration depends on the specific gas mixture used in the experiment.

The experimental data in Fig. 2 are accompanied by results of theoretical model (for details, see [9]). It was shown that admixtures in small quantities enhance the dissociation rate due to a reduction of the wall recombination. Higher admixture concentrations cause a dissociation rate decrease due to volume reactions and admixture recombination mechanism. The rate of increase and decrease and the position of the maximum with respect to the admixture concentration differ for each gas, as the experimental conditions and dissociation and recombination properties of O_2, N_2 and H_2 are different.

Due to different nuclear spin the ^{14}N and ^{15}N isotopes are easily distinguished in ESR spectra. It is interesting that adding of H_2 and O_2 into nitrogen gas causes also different dissociation and recombination rates of ^{14}N and ^{15} isotopes (see Fig. 3).

4 Production of free electrons in afterglow

Change of atomic nitrogen concentration are for the case of oxygen admixture in nitrogen closely followed by the increase of electron density as presented in Fig. 4. The electron concentration was measured by ESR device using the absorption line of electron cyclotron resonance. Taking into account, that free electrons produced in the discharge can not reach such late positions in afterglow, we may deduce, that atomic nitrogen (most probably excited in upper electronic states) plays an important role in production of electrons in the afterglow [8].

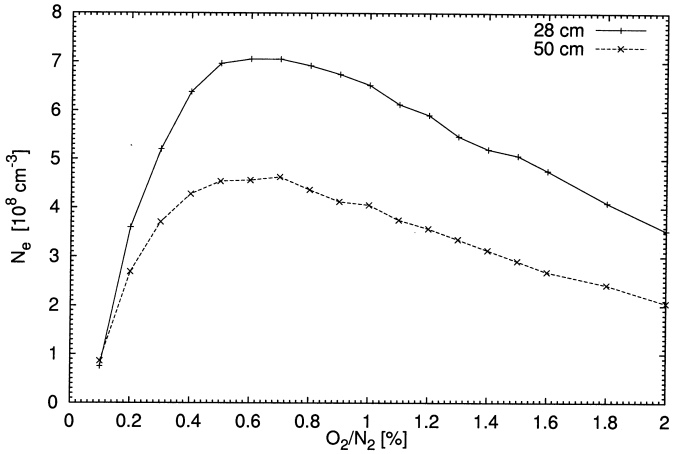

Fig. 4. Dependence of electron density on O_2 admixture for two positions in afterglow (distance of ESR cavity from RF discharge was 28 and 50 cm). Nitrogen flow was 50 sccm and pressure 450 Pa.

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References

[1] A.A. Westenberg: *Prog. React. Kinet.* **7** (1973) 23

[2] N.M. Johnson, J. Walker, C.M. Dolond, K. Winter, R.A. Street: *Appl. Phys. Lett.* **54** (1989) 1872

[3] J. Janča, A.Tálský, V. Zvoníček: *Plasma Chem. And Plasma Process.* **16** (1996) 187

[4] M. Janča, J. Janča, V. Kudrle, A. Tálský: in *Proc. 14th Internat. Symp. Plasma Chem.*, Prague 1999. (Eds. M. Hrabovský, M. Konrád, V. Kopecký), Prague 1999, p. IV-1843

[5] N.M. Johnson, J. Walker, K.S. Stevens: *J. Appl. Phys.* **69** (1991) 2631

[6] J. Janča, M. Janča, A. Tálský, V. Zvoníček: in *Proc. 13th Internat. Symp. Plasma Chem.*, Peking 1997. (Ed. C.K. Wu) 1997, p. I-76.

[7] N.M. Johnson, P.V. Santos, J. Walker, K.S. Stevens: *Mater. Res. Soc. Symp. Proc.* **219** (1991) 703

[8] V. Kudrle, A. Tálský, J. Janča: in *Proc. 14th Inter. Symp. Plasma Chem.*, Prague 1999. (Eds. M. Hrabovský, M. Konrád, V. Kopecký), Prague 1999, p. II-723

[9] V. Kudrle, A. Tálský, A. Kudláč, V. Křápek: *Czech. J. Phys. S3* **50** (2000) 305