

ORGANOSILICON REACTIONS WITH ATOMS: HMDSZ + N

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Received 3 April 2003, accepted 15 Aug. 2005

Plasma containing hexamethyldisilazane (HMDSZ) and nitrogen or ammonia is often used to deposit silicon nitride-like films at low substrate temperature. Kinetics of the reaction $N + \text{HMDSZ}$ was studied by means of the electron paramagnetic resonance (EPR) method. Molecular nitrogen was partially atomised by a 13.56 MHz discharge in the quartz tube which passed through an EPR cavity. HMDSZ vapours were injected between the discharge and EPR cavity. N-atom loss occurring due to the reaction of atomic nitrogen with HMDSZ molecules was measured and the relevant rate coefficient k was determined. The results could be used for the deposition process optimisation and modelling.

PACS: 52.20.Hv, 52.70.Gw, 82.20.Pm, 82.30.Cf

1 Introduction

The processes for the deposition of Si_3N_4 -like films by plasma enhanced chemical vapour deposition (PECVD) of hexamethyldisilazane (HMDSZ) in radiofrequency or microwave plasma reactors are used for synthesis of amorphous materials [1–4]. Deposited films are silicon nitride-like, they contain carbon but nearly no oxygen. Coatings have some very good properties, e.g. they are hard and chemically very resistant [1, 3]. HMDSZ plasma-polymerised thin films possess a very low permeability coefficient for O_2 and N_2 . The dissolution and etch rate of silicon nitride thin films prepared from HMDSZ are negligible [1].

In the present study for Si_3N_4 -like material synthesis monoatomic nitrogen is mixed downstream of the remote RF plasma reactor with stable molecular species (HMDSZ – see Fig.1). The mixing is intended to introduce primarily chemical reaction that yields a reactive product, commonly termed the gas-phase precursor, to promote Si_3N_4 -like film deposition at moderate temperatures. Monoatomic nitrogen acts as radical scavenger, decreasing the polymerisation rate of organic radicals [5]; nitrogen reacts with HMDSZ in the gas phase, increases its conversion and fragmentation, and removes parts of the organic fraction of the film by means of gas-surface reactions. In the present study the electron paramagnetic resonance (EPR) flow tube technique has been applied to measure absolute concentration of atomic nitrogen. Study of reaction kinetics by EPR was described in detail in [6, 7]. Gas phase chemical reactions for deposition of a-Si:H, a-SiC:H and SiO_2 -like materials in a remote hydrogen and oxygen plasma reactor have been quantitatively characterised with EPR in [8–11].

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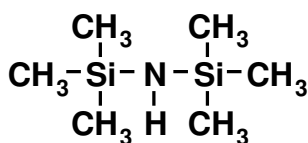


Fig. 1. Molecule of hexamethyldisilazane (HMDSZ).

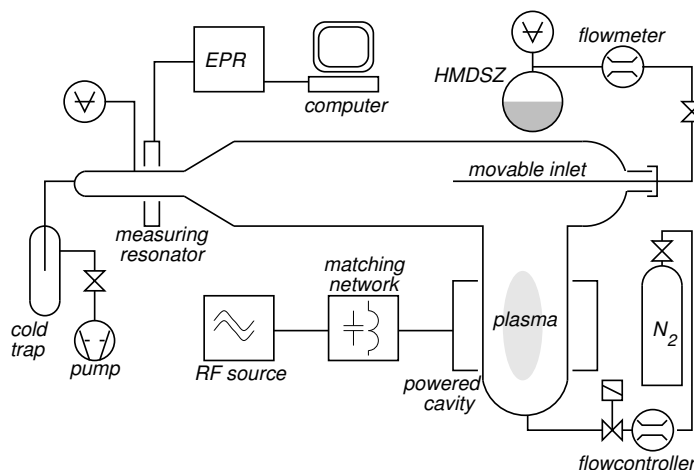


Fig. 2. Experimental setup.

2 Experiment

Schematic drawing of the experimental apparatus is presented in Fig.2. A radiofrequency electrodeless discharge was sustained in the quartz tube with inner diameter of 37 mm by RF generator working at 13.56 MHz. Relatively low power (25 W) was fed into the plasma to maintain the discharge within the cavity; this prevents possible presence (due to backdiffusion) of HMDSZ vapours in the active discharge. Main gas (99.998% nitrogen) was fed from a standard gas bottle through a reduction valve and a mass flow controller. In the discharge the nitrogen was partially atomised and passed through the right-angle bend into EPR measuring resonator (X-band) of EPR spectrometer Zeiss ER9. The density of N atoms in the distance of 35 cm from the discharge reached more than 10^{15} cm^{-3} .

Between the discharge and the measuring resonator the HMDSZ vapour was injected into the flux of partially atomised nitrogen via small-diameter tube. The vapour flow rate (order of several sccm) was controlled by needle valve and measured by pressure drop on a capillary. The distance between the injector and the EPR resonator could be varied over a limited range from 10 to 30 cm. Because of the fact that the distance from the discharge was as much as 10 times higher than the tube diameter, the back diffusion could be neglected. The total pressure in the EPR resonator during all measurements was maintained at 165 Pa (it corresponds to flow rate of 50 sccm). This relatively low pressure was maintained because a higher HMDSZ pressure than N_2 pressure and constant pressure gradient were necessary in our experiment for ensuring steady HMDSZ flow. HMDSZ pressure in the monomer flask was given by the vapour pressure above the HMDSZ surface, which was a function of liquid HMDSZ temperature ($p_{\text{HMDSZ}} \approx 2 \text{ kPa}$ at 20°C), and the temperature of the feeding tubes. The EPR spectrometer was calibrated with molecular oxygen as described in [6]. All measurements were carried out in a flow regime.

3 Measurements and results

EPR measurements provided absolute values of atomic nitrogen concentration [N] and the correction for the loss of [N] by processes that were first order in [N] and independent of HMDSZ, such as diffusion followed by wall recombination. By adjusting the concentrations of the reactants so that $[N] \ll [HMDSZ]$, the second-order (bimolecular) reaction law was reduced to pseudo-first order. The first step of the chemical reaction generally involves CH_3 , CH and NH abstraction from stable HMDSZ molecule to form a free radical.

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

For the case without flowing HMDSZ we can write for the N-atom concentration

$$\frac{d[N]_{\text{off}}}{dt} = -k_{\text{loss}} \cdot [N]_{\text{off}}, \quad (1)$$

where k_{loss} is the wall recombination coefficient (second-order reactions were not considered because of their insignificant role in our experiment). From this equation we get

$$[N]_{\text{off}} \cdot \frac{[N_2]_0}{[N_2]_x} = C_1 \cdot \exp(-k_{\text{loss}}t), \quad (2)$$

where C_1 is a constant depending on the experimental arrangement and the term $[N_2]_0/[N_2]_x$ compensates the N-atom concentration decrease due to pressure decrease along the tube.

For the case with flowing HMDSZ

$$\frac{d[N]_{\text{on}}}{dt} = -(k_{\text{loss}} + k \cdot [HMDSZ]) \cdot [N]_{\text{on}}, \quad (3)$$

where k is the coefficient of the reaction $N + HMDSZ$. We obtain

$$[N]_{\text{on}} \cdot \frac{[N_2]_0}{[N_2]_x} = C_2 \cdot \exp\left(- (k_{\text{loss}} + k \cdot [HMDSZ]) \cdot t\right), \quad (4)$$

where C_2 is constant given by experimental conditions. By dividing (4) and (2) and taking the logarithm of both sides we have

$$\ln\left(\frac{[N]_{\text{on}}}{[N]_{\text{off}}}\right) = C_3 - k \cdot [HMDSZ] \cdot t. \quad (5)$$

Time of residence t may be determined from known pressure, flow rate and discharge tube diameter. Therefore, principally two types of experiment may be carried out:

- keeping [HMDSZ] constant and moving the injector (varying t),
- residence time t fixed, varying HMDSZ flow rate.

Our measurements (see Fig.3) were performed at constant flow rate of HMDSZ, corresponding to $[HMDSZ] = 2.48 \cdot 10^{15} \text{ cm}^{-3}$. The distance between the injector and EPR resonator was varied from 10 cm up to 26 cm, i.e. the time of residence was in the range 0.12 – 0.32 s. Using the relation (5) we obtain

$$k = 7.3 \cdot 10^{-16} \text{ cm}^3 \text{ s}^{-1}. \quad (6)$$

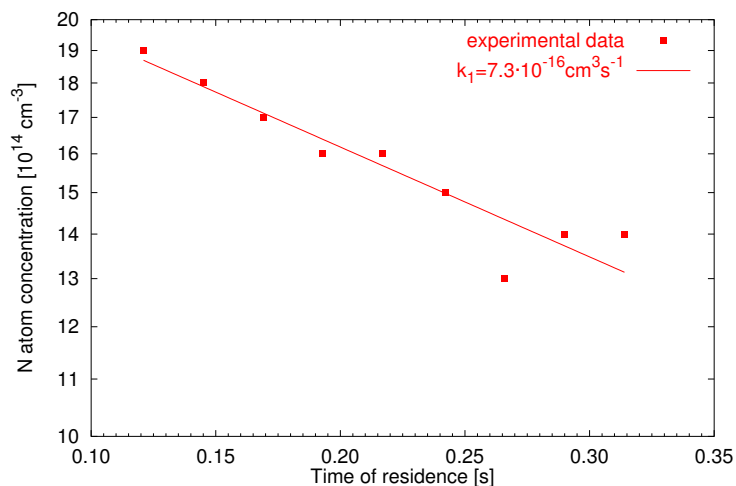


Fig. 3. Variation of N-atom concentration (in logarithmic scale) with the time of residence. HMDSZ flow rate $Q_{\text{HMDSZ}} = 3.86$ sccm. N_2 flow rate was maintained at 50 sccm.

4 Conclusion

The rate coefficient for the reaction of HMDSZ with atomic nitrogen was measured by means of the remote RF plasma reactor and the EPR technique. These experiments yield the rate coefficient of the reaction $\text{N} + \text{HMDSZ}$ around $7 \cdot 10^{-16} \text{ cm}^3 \text{ s}^{-1}$.

However there exists an uncertainty of the residence time t due to decrease in discharge tube diameter just in front of measuring resonator. Better results may be obtained using difference method.

Acknowledgement: This work was supported by Ministry of education MSM 143100003, Grant agency GACR 202/01/P106 and by COST 527.20.

References

- [1] J. Janča, M. Nečasová, T. Šíkola: *Acta Phys. Slov.* **33** (1983) 187
- [2] F. Fracassi, R. d'Agostino, P. Favia: *Plasma Sources Sci. Technol.* **1** (1993) 1
- [3] F. Fracassi, R. d'Agostino, G. Bruno: *Plasmas and Polymers* **1** (1996) 3
- [4] F. Fracassi, R. Lamendola: *Plasmas and Polymers* **2** (1997) 25
- [5] A. Ricard: *Reactive plasmas* (SFV Paris) 1996
- [6] A. A. Westenberg, N. de Haas: *J. Chem. Phys.* **40** (1964) 3087
- [7] A. A. Westenberg: *Prog. React. Kinet.* **7** (1973) 23
- [8] N. M. Johnson, J. Walker, C. M. Dolond, K. Winter, R. A. Street: *Appl. Phys. Lett.* **54** (1989) 1872
- [9] N. M. Johnson, P. V. Santos, J. Walker, K. S. Stevens: *Mater. Res. Soc. Symp. Proc.* **219** (1991) 703
- [10] N. M. Johnson, J. Walker, V. Stevens: *J. Appl. Phys.* **69** (1991) 2631
- [11] J. Janča, A. Tálský, V. Zvoníček: *Plasma Chemistry and Plasma Processing* **16** (1996) 187