Influence of HMDSO admixtures on the discharge characteristics of a barrier discharge in argon for thin film deposition

M. M. Becker[1], J. Philipp[2], C.-P. Klages[2], F. Sigeneger[1], D. Loffhagen[1]

[1]*INP Greifswald, Felix-Hausdorff-Str. 2, 17489 Greifswald, Germany*
[2]*TU Braunschweig, Pockelsstr. 14, 38092 Braunschweig, Germany*

The influence of small admixtures of HMDSO on the discharge behaviour of an atmospheric pressure dielectric barrier discharge in argon used for deposition of silicon-organic films is analysed experimentally and by numerical calculations. A marked decrease of the burning voltage with increasing HMDSO concentration in the range of 0 . . . 200 ppm is observed in the experiment and confirmed by the fluid model. The theoretical investigations point out that the drop of the burning voltage as well as the change of the discharge behaviour is caused by a strong increase of the Penning ionization rate with increasing HMDSO content.

1. Introduction

Dielectric barrier discharges (DBD) are widely used for deposition of functional silicon-organic films by plasma enhanced chemical vapour deposition (PE-CVD) processes [1–4]. For film deposition, the discharge is ignited in a carrier gas mixed with small amounts of a precursor gas. Common precursors for the deposition of SiO_x containing films are tetraethoxysilane (TEOS), tetramethylsilane (TMS), and hexamethyldisiloxane (HMDSO $\equiv (CH_3)_3SOSi(CH_3)_3$) [5].

It has been found that even small admixtures of the precursor gas required for the PE-CVD process can influence the characteristics of the discharge [4, 6]. For example, Penning ionization is known to reduce the breakdown voltage in so-called Penning mixtures significantly [4].

A similar effect has been observed in the present investigations of a DBD in argon with small admixtures of HMDSO. It has been found experimentally that the amount of HMDSO influences directly the burning voltage as well as the current-voltage characteristics of the discharge. In order to clarify the basic processes responsible for the observed phenomena, the experimental studies have been complemented by numerical calculations.

2. Experimental setup

The discharge experiments were realized using a DBD reactor. A schematic of the experimental setup is presented in figure 1.

The DBD was ignited between two plane parallel electrodes separated by a discharge gap of 1 mm. Both electrodes were made of steel mesh glued with epoxy on the surface of glass plates with a thickness of 2 mm. For film deposition experiments, electrodes with an area of 80 cm^2 have been used. Here, the electrode area was reduced to 1 cm^2 to assure a well-defined HMDSO concentration in the discharge area.

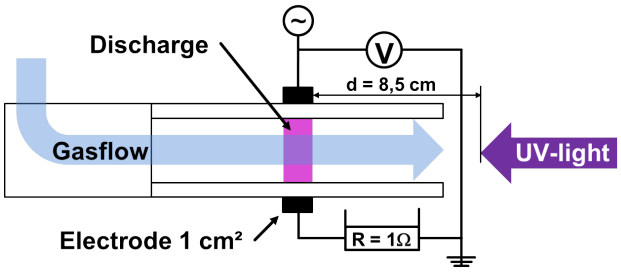

Figure 1: Side view of the experimental setup (schematics not to scale). V and R denote positions of the high voltage probe and the shielded shunt resistor used for current measurements.

A high voltage pulse generator (G2000, Redline Technologies) was used to power the DBD with 87 kHz sinusoidal voltage. A source of ultraviolet light (VL-6.C, Vilber Lourmat) with a wavelength of 254 nm and a power of 6 W was placed in front of the discharge gap to raise the initial electron density.

Voltage and current signals during the discharge were monitored by an oscilloscope (Tektronix MDO 3052) equipped with a high voltage probe (Datatec PHV 4002-3). The voltage was raised stepwise during the investigation of the external burning voltage for a specific concentration of HMDSO until the discharge was ignited and covered the whole electrode area. For cur-

rent measurements the voltage amplitude was set to 3 kV and the HMDSO/Ar mixture of interest was fed to the reactor.

In order to analyse the influence of the concentration of HMDSO on the discharge characteristics, different amounts of HMDSO were admixed to the total argon gas flow rate between the plates, which has been adjusted to 3 slm. The investigated HMDSO concentrations were 0, 4.4, 10, 22, 110 and 220 ppm, respectively, calculated for a HMDSO vapour pressure of 44 mbar at 20° C room temperature [7].

3. Fluid modelling approach

In order to describe theoretically the ignition and spatiotemporal development of the discharge between the dielectrics, a time-dependent, spatially one-dimensional fluid model has been used. The modelling approach comprises the continuity equations for all relevant argon species, the electron energy balance equation, Poisson's equation for the self-consistent determination of the electric field and an equation for balancing the surface charges accumulating at the dielectrics as detailed in [8]. Here, the improved drift-diffusion approximation introduced in [9] has been used for the description of the electron particle and energy transport.

The influence of the HMDSO admixture on the plasma behaviour is described by the collision processes most relevant for the ionization budget of Ar plasmas with small amounts of HMDSO. Namely, electron impact ionization of HMDSO leading to the generation of pentamethyldisiloxanyl ions ($PMDSl^+$) and methyl radicals (CH_3), the generation of $PMDSl^+$ due to charge transfer processes, Penning ionization according to the process

$$Ar^* + HMDSO \rightarrow PMDSl^+ + CH_3 + Ar + e \quad (1)$$

as well as quenching of excited argon species in collisions with HMDSO and electron-$PMDSl^+$ recombination are considered in the reaction kinetic model.

3. Results and discussion

In the following results of measurements and numerical modelling are represented.

3.1 Current and voltage measurements

The variation of the external burning voltage

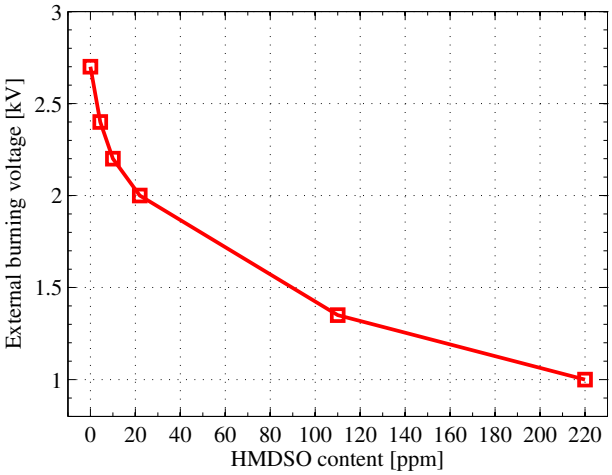

Figure 2: Measured external burning voltage in dependence on the HMDSO concentration.

U_b^{ext} with changing HMDSO content is shown in figure 2. For HMDSO concentrations from 0 to 20 ppm a sharp decrease of U_b^{ext} appears, which becomes smoother for higher admixtures of HMDSO. A drop of U_b^{ext} by more than a factor of two can be stated for 220 ppm HMDSO.

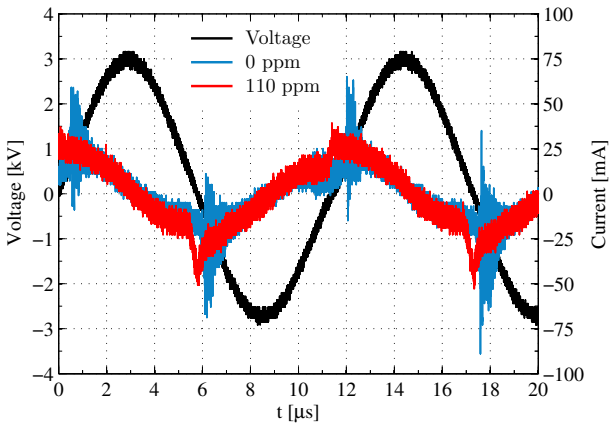

Figure 3: Measured voltage and current for pure argon and Ar + 110 ppm HMDSO.

As illustrated in figure 3, the admixture of HMDSO to the argon plasma does not only influence the burning voltage but has a strong influence on the temporal variation of the discharge current, too. In pure argon, the current signal exhibits strong oscillations during ignition of the microdischarges. Admixture of 110 ppm HMDSO causes the transition to a more regular evolution of the discharge current with temporally earlier and slightly smaller current peaks. The results of the current measurements suggest that the admixture of HMDSO to the argon discharge

causes a homogenization of the discharge and transition to a transient glow discharge. The transition from a filamentary discharge in pure argon to a diffuse discharge in Ar-HMDSO gas mixtures is also confirmed by optical emission.

3.2 Numerical results

In order to reveal the physical effects responsible for the change of the discharge behaviour with changing HMDSO content, numerical calculations have been performed for the experimental conditions assuming a constant gas temperature of 300 K. The voltage amplitude was increased to 4 kV to achieve ignition of the DBD for all HMDSO concentrations considered. Time-periodic results for all quantities have been obtained by tracing the temporal evolution of the discharge for several periods.

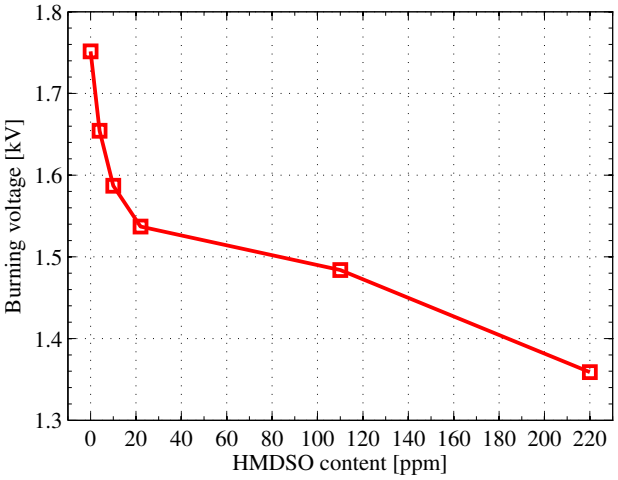

Figure 4: Calculated internal burning voltage in dependence on the HMDSO concentration.

Figure 4 represents the burning voltage determined by modelling for different HMDSO concentrations. Note that the amplitude of the external voltage source was not changed throughout the calculations. The *internal* burning voltage U_b^{int} shown in this figure represents the amplitude of the gap voltage predicted for different HMDSO concentrations. In agreement with the experiments, a decrease of the burning voltage with increasing HMDSO content is obtained.

In figures 5 and 6 the temporal evolution of the gap voltage and the discharge current density as well as the spatiotemporal variation of the electron density are shown for pure argon and a HMDSO concentrations of 110 ppm, respectively. In both cases the numerical results exhibit one

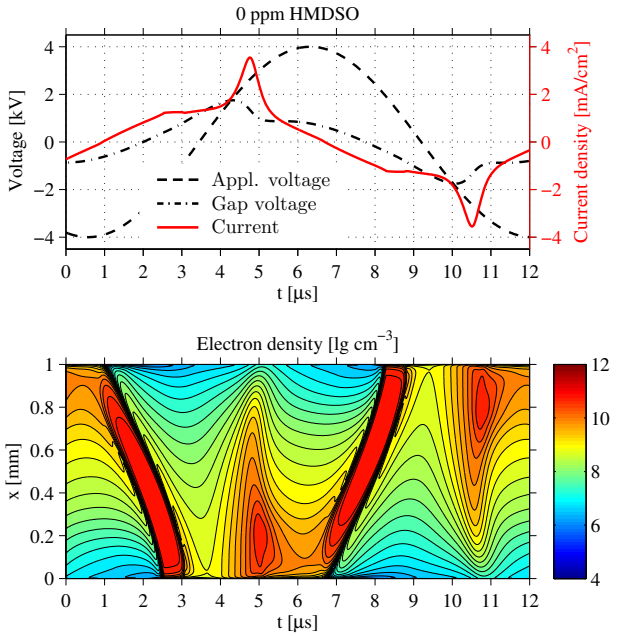

Figure 5: Temporal variation of voltage, current and electron density in pure argon.

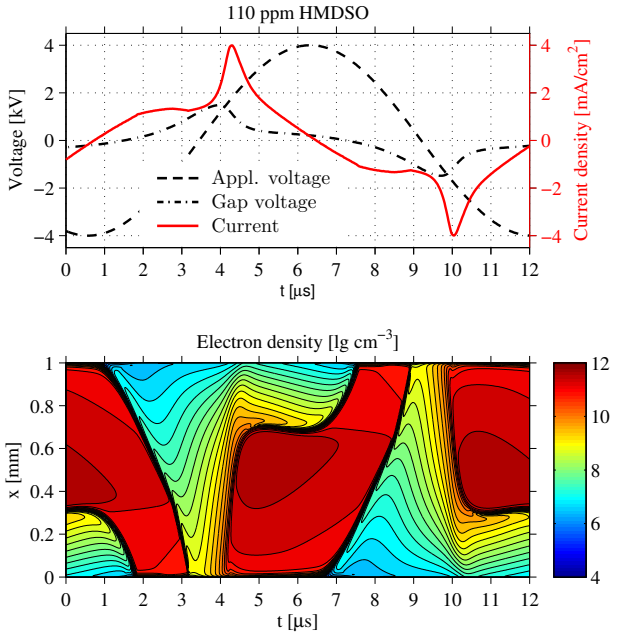

Figure 6: Temporal variation of voltage, current and electron density in Ar + 110 ppm HMDSO.

current peak per half-period of the order of 1 to 10 mA/cm^2 that extends over a time of about 1 µs. These current densities and time scales are characteristic of glow like discharges [4].

In pure argon the spatiotemporal distribution of the electron density (see figure 5) shows the periodic repetition of transient glow discharges. After reversal of the electric field at $t \approx 1$ µs the elec-

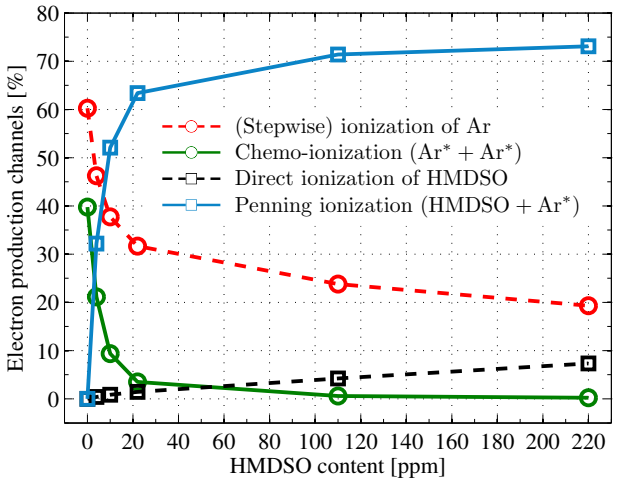

Figure 7: Influence of the HMDSO content on the contribution of the different ionization processes to electron production.

trons are accelerated towards the instantaneous anode at $x = 0$ and get partially absorbed. Then, new electrons are created in ionization processes and due to the emission of secondary electrons at the instantaneous cathode located at $x = 1\,\mathrm{mm}$ (Townsend pre-phase). In the span from 4 to 5 µs a Townsend to glow transition takes place. The glow region expands over about 1/2 of the gap.

The admixture of 110 ppm HMDSO causes a change of the discharge behaviour as shown in figure 6. The electron density increases, the glow region gets more pronounced expanding over about 2/3 of the gap and a shortening of the Townsend pre-phase takes place. In agreement with the measured current signal, the current maxima occur slightly earlier compared to pure argon.

The reason for the change of the discharge characteristics with increasing HMDSO content is revealed by looking at the relative contribution of the different electron production channels represented in figure 7. In pure argon, electrons are mainly created in ground and stepwise ionization processes (60 %) with a smaller contribution resulting from chemo-ionization in collisions of excited argon atoms (40 %). Since the ionization energy of the HMDSO molecule (9.6 eV) is smaller than the energy of the metastable argon atoms (11.6 eV), the admixture of HMDSO is accompanied especially by the additional generation of electrons due to Penning ionization according to reaction (1). Here, Penning ionization gets the predominant electron source for HMDSO concentrations larger than about 10 ppm and causes the observed reduction of the burning voltage and the change of the discharge characteristics.

4. Summary

The influence of HMDSO admixtures on the discharge characteristics of an argon DBD used for deposition of silicon-organic films has been analysed by experiments and numerical modelling. It has been found that the observed reduction of the burning voltage and the increase of the electron density with increasing HMDSO content is caused by an efficient generation of electrons in Penning ionization processes as soon as small amounts of few ppm of HMDSO are added to the argon plasma.

Acknowledgment

This work was supported by the German Research Foundation under grants LO 623/3-1 and KL 1096/23-1.

References

[1] R. Foest, F. Adler, F. Sigeneger, M. Schmidt, *Surf. Coat. Technol.* **163–164** (2003) 323–330.

[2] C.-P. Klages, C. Berger, M. Eichler, M. Thomas, *Contrib. Plasma Phys.* **47** (2007) 49–56.

[3] D. Trunec, L. Zajíčková, V. Buršíková, F. Studnička, P. Šťahel, V. Prysiazhnyi, V. Peřina, J. Houdková, Z. Navrátil, D. Franta, *J. Phys. D: Appl. Phys.* **47** (2010) 225403.

[4] F. Massines, Ch. Sarra-Bournet, F. Fanelli, N. Naudé, N. Gherardi, *Plasma Process. Polym.* **9** (2012) 1041–1073.

[5] V. Raballand, J. Benedikt, S. Hoffmann, M. Zimmermann, A. von Keudell, *J. Appl. Phys.* **105** (2009) 083304.

[6] N. Jidenko, C. Jimenez, F Massines, J.-P. Borra, *J. Phys. D: Appl. Phys.* **40** (2007) 4155–4163.

[7] R. Abbas, A. Schedemann, C. Ihmels, S. Enders, J. Gmehling, *Ind. Eng. Chem. Res.* **50** (2011) 9748–9757.

[8] M. M. Becker, T. Hoder, R. Brandenburg, D. Loffhagen, *J. Phys. D: Appl. Phys.* **46** 355203.

[9] M. M. Becker, D. Loffhagen, *AIP Advances* **3** (2013) 012108.