Diagnostics of particle forming process plasmas

P. Sadler, M. Hundt, H. Kersten
IEAP, University of Kiel, Kiel, Germany

Introduction

Under certain process conditions formation of nano- and micro-particles (dust) can be observed in reactive process plasmas used in etching, deposition, or modification of solid surfaces. The nucleation and growth of the nanodust grains in plasmas were observed and studied previously by several authors [1-3]. Nanoparticle growth is usually a very fast and complex multi-stage process which is difficult to monitor. Most of the present-day diagnostic techniques still lack reliability and require further development. For an improved insight in the plasma-polymerization processes, especially to determine the key precursors in the carbonaceous dusty plasmas, mass spectrometry has been successfully used by several research groups [4,5]. Nevertheless, a quantitative mass spectrometry is a very complex technique.

In order to investigate the involved mechanisms for the generation of nano-particles and their incorporation into thin films as well as for the modification of powder particles often organic precursors (C_2H_2, HMDSO etc.) are used as additional species in process plasmas. In general, it is rather difficult to measure the converted quantity of these precursors directly. However, real-time monitoring of the gas and plasma parameters (pressure, density, chemical composition) in the discharge where the nanodust nucleates and grows is a highly desirable challange. Besides, these measurements are extremely complex for the molecular plasmas which are increasingly used in the nanomaterial synthesis technology due to their extraordinary reactivity and other favorable characteristics [6]. One possibility is montoring of by-products of particle formation by absorption spectroscopy – an example will be shown in this paper.

Experimental

In the present experiments the time-dependent formation of dust particles in a capacitively coupled asymmetric rf-discharge containing argon and acetylene or HMDSO, respectively, has been studied, see Fig.1 [7]. The precursor concentration has been measured by a special quantum cascade laser absorption spectroscopy technique (QCLAS) to investigate

characteristic absorption lines in the plasma [8]. The behavior of the electron collision rate in the plasma was monitored by self-excited electron resonance spectroscopy (SEERS), too. In context with electrical measurements this leads to an improved understanding of the interaction of particles formed inside the plasma with the discharge.

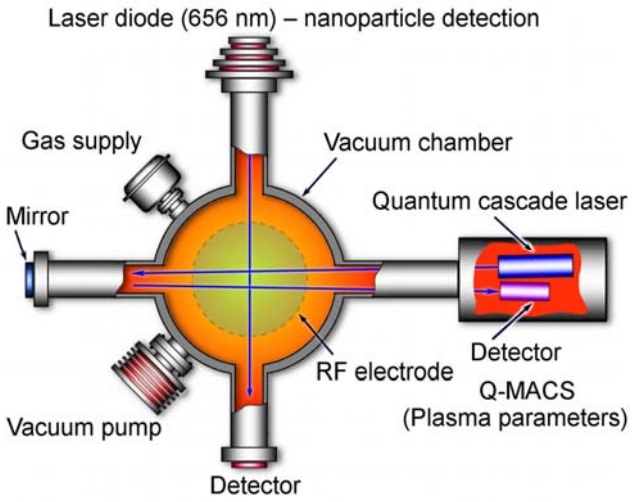

Fig.1: Experimental setup [7].

In addition to plasma diagnostics the chemical composition of deposited micro-particles in HMDSO plasmas has been determined by means of X-ray photoelectron spectroscopy (XPS).

Results and Discussion

Particle formation observed by laser light scattering or transmission, respectively, is related to changes in the original precursor concentration, the total gas pressure and the bias-voltage [7]. Under specific discharge conditions even oscillations in particle growth occur. The period of such oscillations strongly depends on the precursor concentration before ignition of the discharge. Three characteristic regimes in particle formation have been observed: periodic, periodic-continuous and continuous [7]. The combination of various in-situ diagnostics allows for a correlation between plasma parameters and particle generation.

There are two initial paths of fragmentation of HMDSO precursor molecules by electron impact dissociation. Mainly methyl groups are split off leading to methane and, subsequently, acetylene in the gas phase (Fig.2). The fragments often result in the formation of amorphous hydrogenated carbon dust as known in hydrocarbon-containing plasmas [2]. The methane formation is due to hydrogen attachment of methyl groups: $CH_3 + H \Rightarrow CH_4$ (Fig.3 left).

With small addition of oxygen (yellow) the concentration increases slightly. This is accounted to the oxidation reactions [9] of the fragments which indirectly produce H and CH_3 again.

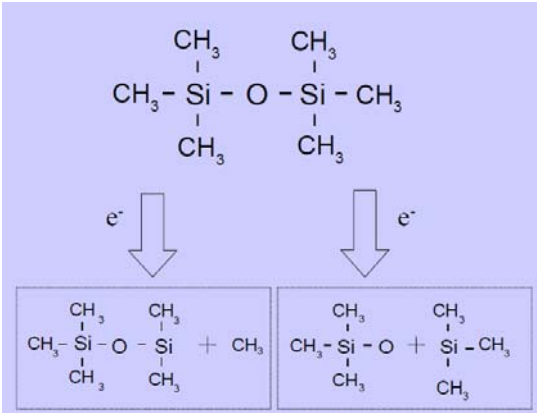

Fig.2: Two dissociation patterns (bottom) for fragmentation of HMDSO (top) by electron impact.

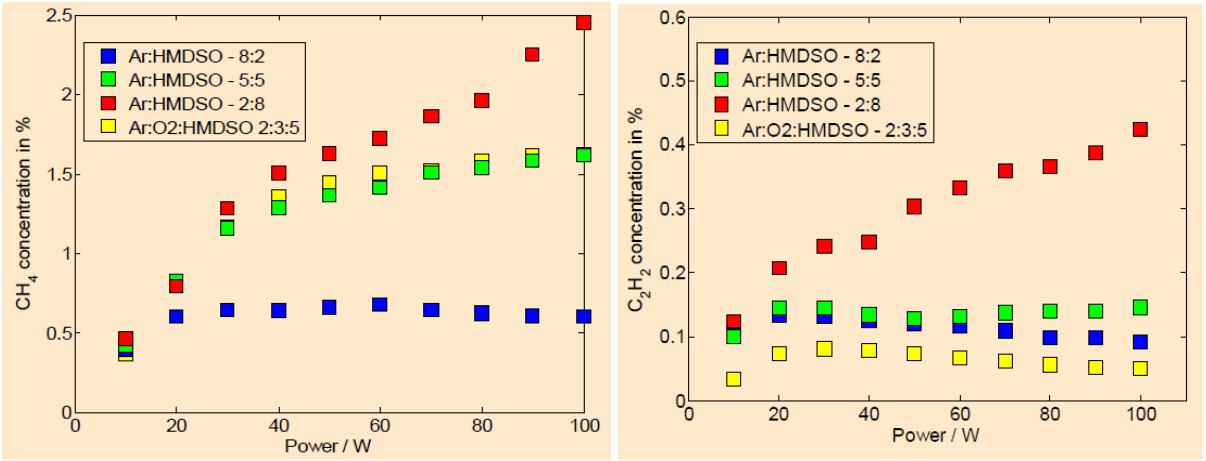

Fig.3: Methane (left) and acetylene (right) concentration during particle formation by HMDSO fragmentation as measured by QCLAS.

Finally, acetylene is produced by hydrocarbon chemistry (Fig.3 right) in the following subsequent reactions:

$$CH_4 + CH \Rightarrow C_2H_4 + H \text{ and } C_2H_4 + e \Rightarrow C_2H_2 + H_2 + e.$$

Here, the addition of oxygen reduces the acetylene concentration by 50% due to oxidation reactions.

The XPS overview spectrum of the collected dust particles is shown in Fig.4. The Si(2p) detail spectrum is fitted at different oxidation steps which indicate the organic content. The

lower the coordination number of oxygen the higher the organic content of the collected particles is. Hence, we generated very carbonaceous SiO particles in the HMDSO process plasma. These experimental results are in good agreement with mass spectrometry measurements of Alexander et al. [10] who obtained high mass molecules mostly as polydimethylsiloxane-like structures (PDMS).

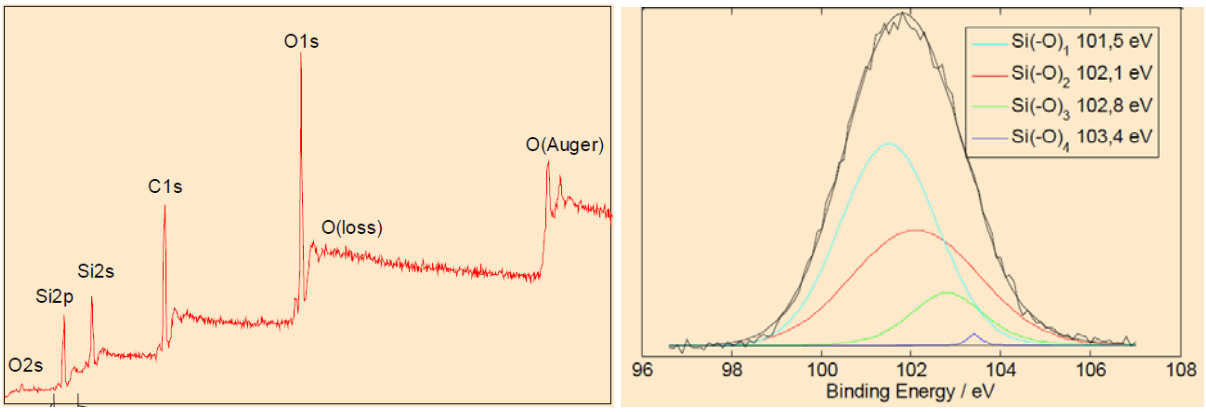

Fig.4: XPS overview spectrum (left) and detailed Si(2p) peak (right) of collected dust particles produced in HMDSO process plasma.

References

[1] K. Ostrikov, Rev. Mod. Phys. **77,** 489 (2005); J. Phys. D: Appl. Phys. **44**, 174003 (2011).

[2] J. Berndt, E. Kovacevic, I. Stefanovic, O. Stepanovic, S.H. Hong, L. Boufendi, and J. Winter, Contrib. Plasma Phys. **49**, 107 (2009).

[3] S. Hong, J. Berndt, and J. Winter, Plasma Sourc. Sci. Technol. **12**, 46 (2003).

[4] I. Levchenko, K. Ostrikov, K. Diwan, K. Winkler, and D. Mariotti, Appl. Phys. Lett. **93**, 183102 (2008).

[5] C. Hollenstein, J.L. Dorier, J. Duta, L. Sansonnens, and A.A. Howling, Plasma Sourc. Sci. Technol. **3**, 278 (1994).

[6] K. Vasilev, A. Michelmore, P. Martinek, J. Chan, V. Sah, H. J. Griesser, and R. T. D. Short, Plasma Proc. Polym. **7**, 824 (2010).

[7] M. Hundt, P. Sadler, I. Levchenko, M. Wolter, H. Kersten, and K. Ostrikov, J. Appl. Phys. **109** (2011), accepted.

[8] S. Welzel, G. Lombardi, P.B. Davies, R. Engelen, D.C. Schram, and J. Röpcke, J. Appl. Phys. **104**, 093115 (2008).

[9] G.F. Leu, A. Brockhaus, and J. Engemann, Surf. Coat. Technol. **174**, 928 (2003).

[10] M.R. Alexander *et al.*, Appl. Surf. Sci. **137**, 179 (1999).