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# MINIATURIZED ATMOSPHERIC PRESSURE PLASMA JET (APPJ) FOR DEPOSITION OF $SIO_X$ FILMS WITH DIFFERENT SILICON-ORGANIC COMPOUNDS – A COMPARATIVE STUDY

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**Abstract.** Thin films are deposited by means of an APPJ, driven at 27.17 MHz with Ar and small admixtures (0.5 ppm) of silicon organic compounds as thin film precursor. Static deposition experiments have been performed. The radial dependence of these characteristic footprints is evaluated for films from hexamethyldisiloxane ($Si_2OC_6H_{18}$, HMDSO) and octamethylycyclodisiloxane ($Si_4O_4C_8H_{24}$, OMCTS). The films are evaluated with FT-IR and XPS and compared with regard to their chemical composition. The results of both analytical methods reveal a consistent picture.
Films from HMDSO and OMCTS and the APPJ in locked mode show no IR absorption of $CH_2$ and $CH_3$ bands. The highly cross-linked $SiO_x$ films from OMCTS along with position and appearance of the O-Si-O peak (FT-IR) signify potential for films with enhanced scratch resistance.

## 1. Introduction

Silicon-organic compounds are widely used as starting substance for the deposition of thin films by PE-CVD techniques. Both, their chemical composition and the particular plasma-physical deposition conditions influence the chemical composition and the appearance of the film (e.g. morphology, internal stress, refractive index). Therefore, films with varying film properties can be deposited that address a broad range of applications: from protective layers against corrosion, over adhesion control to diffusion barriers.

Next to traditional, low pressure techniques, normal pressure plasmas have been employed successfully for surface treatment. The use of a miniaturized APPJ, compared to other non-equilibrium, normal pressure plasmas, is advantageous in particular for local film deposition or for the coating of 3D forms e.g. inner walls of wells, trenches or cavities. The jet geometry offers the advantage that the surfaces to be treated are not placed between electrodes thus allowing better flexibility in terms of substrate distance and electrical field [1,2].

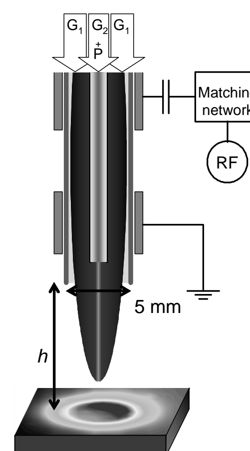

**Fig. 1** Scheme of APPJ

However, films deposited under normal pressure tend to a less favourable content of carbon ($CH_2$, $CH_3$ groups, amorphous carbon) and a comparably low degree of cross-linking along with an implementation of low molecular constituents (water, hydroxyl groups) in the polymer network. In the present work, films are deposited with the recently observed homogenized plasma mode (locked mode) which is characterized by regularly ordered and moving discharge filaments [3]. It is investigated if these conditions can lead to

films that overcome the limitations above and produce $SiO_x$ films with a high degree of cross-linkage and low carbon content. Moreover, it is evaluated, whether the specific precursor molecule [4] - next to the proper selection of discharge parameters – can influence the film properties.

Static deposition experiments produce a characteristic deposition profile of the plasma source (foot print) [5]. The knowledge of the film properties over the profile of the foot print is essential to allow for a controlled deposition of larger areas with the source moving relative to the substrate.

## 2. Experimental

The plasma source (figure 1) has been described elsewhere [3] It features two nested quartz capillaries. The precursor-containing gas mixture (inner channel: Ar (2.0 slm) + $O_2$ (2.0 sccm) + Precursor (HMDSO/ OMCTS, 0.05 g/h) is introduced via the inner capillary downwards of the discharge. Ar (0.8 slm) is fed into the outer channel. Two ring electrodes are attached to the outer quartz capillary. The upper electrode is capacitively coupled to the RF generator (27.12 MHz) over a matching network. The lower electrode is connected to ground. The RF power, measured at the generator output is 6W.

The local deposition is carried out with the plasma source pointing perpendicularly to the electrically floating surface at a distance of 6 mm. The surface remains at room temperature (20 – 30 $^{o}$C). During the deposition, a characteristic film profile builds up (figure 1). At deposition rates between 10 and 45 nm/min, typical deposition times of 30 min are required to ensure a film thickness sufficient for FT-IR analysis. Deposition experiments were carried out with the plasma source in locked mode.

Samples of polycarbonate, glass, Ti platelets, and Al foil served as substrate during deposition. Moreover, potassium bromide (KBr) samples where used to provide a better contrast for surface analysis.

Scanning X-ray photo electron spectroscopy (XPS, Kratos analytical Axis Ultra,) and Fourier transform infrared absorption (FT-IR) spectroscopy (Perkin Elmer, Spectrum Spotlight 200 microscope) provide space resolved information on the chemical composition over the foot print area.

## 3. Results and Discussion

*Deposition with HMDSO*

Figure 2 (a,c,e) shows FT-IR spectra for different radial positions of the foot print. A dominating OSiO at 1070 $cm^{-1}$ (ASM, in phase) is observed throughout the whole foot print. The shift from 1000 $cm^{-1}$ to 1070 $cm^{-1}$ indicates an increase of the $SiO_x$ stoichiometry. The longitudinal optical (LO) at 1200 $cm^{-1}$and the transverse optical (TO) modes of OSiO ($LO_4$-$TO_4$ pair [6,7]) at 1130 $cm^{-1}$ (out of phase, “surface mode”) are a symptom of altered porosity and compressive stress of the films and occur only in the periphery of the footprint (figure 3 a,e). Moreover, the bending vibration of SiO at 808 $cm^{-1}$ along with stretching vibrations of SiOH (930 $cm^{-1}$) and OH (3300 $cm^{-1}$) are present in the spectrum. The latter two are caused by water contaminations and hydroxyl groups. In general, for the radial dependence from

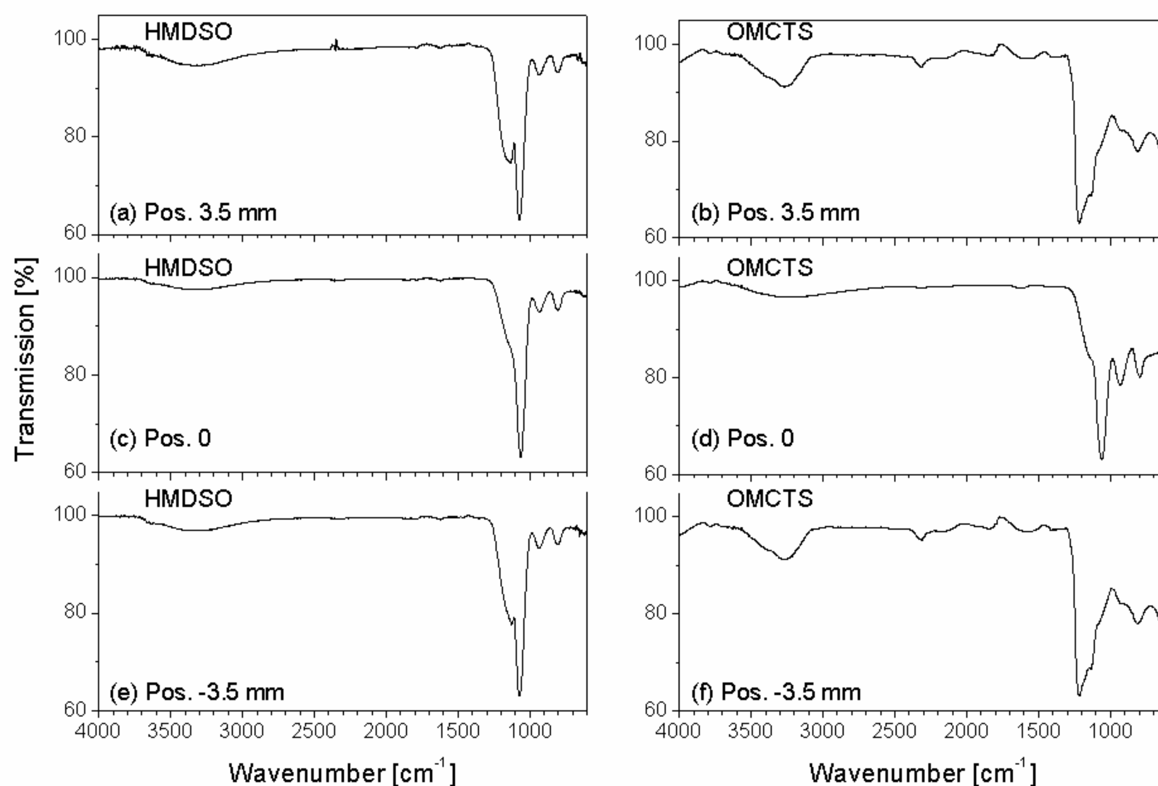


**Fig. 2** FT-IR spectra for films from HMDSO and OMCTS. The positions are representative of different radial distances from the center of the foot print.

center to periphery a transition of the intensity of the bands from the ASM over the $TO_4$ to the $LO_4$ and an increase of the OH related peaks is noted.

The percentage of different Si-O constitutions resulting from the analysis of the high resolved Si 2p peak (XPS) is shown in figure 3a. The oxygen-rich components $(Si(-O)_4$ and $Si(-O)_3)$ prevail over the whole spot with a special emphasis in the spot centre. Accordingly, a slight increase of the polymer bond components $(Si(-O)_1$ and $Si(-O)_2)$ towards the outer region is obtained. The binding constitution is positively correlated to the ratio Si:C. A stoichiometry Si:O of 0.45 (quartz like) is concentrated in the central area (figure 3b).

*Deposition with OMCTS*

FT-IR measurements demonstrate that a ASM of OSiO at 1070 $cm^{-1}$ along with stretching vibrations of SiOH (930 $cm^{-1}$) is observed for the central area of the spot exclusively (figure 2d), whereas in the surrounding area (r=3.5 mm) a dominating $LO_4$-$TO_4$ pair at 1130 $cm^{-1}$ and 1200 $cm^{-1}$ is obtained with a maximum at the LO band (figure 3 b,f). The bending vibration of SiO at 808 $cm^{-1}$ appears throughout the whole range. The stretching vibration of OH (3300 $cm^{-1}$) occurs preferably in the outer region.

The inorganic bond components $(Si(-O)_4$ and $Si(-O)_3)$ dominate even more and only a negligible part (below 4%) of polymer bond components $(Si(-O)_1$ and $Si(-O)_2)$ is present (figure 3c). The foot print is characterized by a very homogeneous chemical configuration and elemental composition (figure3 b,d) and a lower C content (below 5%) in the film compared to HMDSO 13%).

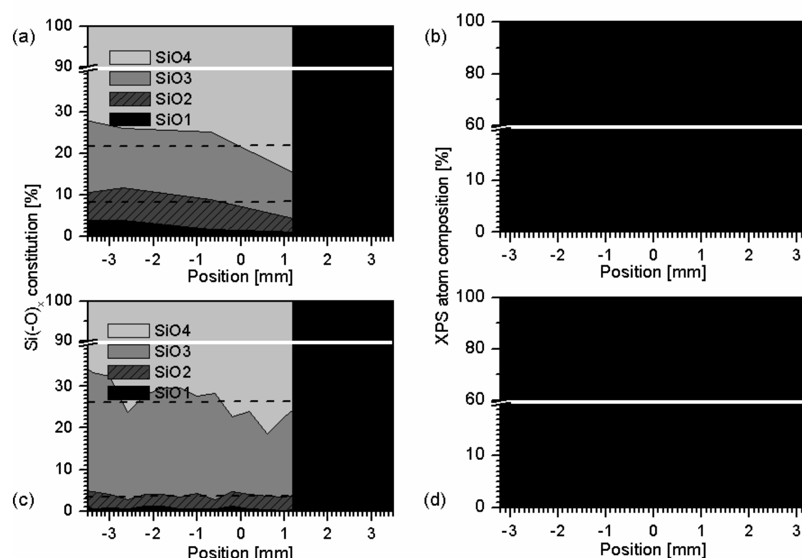


**Fig. 3** Radial dependence of Si $(-O)_x$ chemical constitution and of the XPS atom composition (without hydrogen) across the foot print for HMDSO and for OMCTS. Center of foot print at position 0 mm.

## 4. Conclusion

A comparative study of the $SiO_x$ deposition from two different compounds (HMDSO and OMCTS) has been carried out to evaluate the local dependence of the chemical composition (XPS) and constitution (FTIRS) of the films. Both precursors lead to films with a comparably low carbon content. No hydrocarbons bound ($CH_2$ and $CH_3$) within the structure could be detected. Furthermore, the presence of ASM at 1070 $cm^{-1}$ indicates that the stoichiometry of the films (Si:O = 0.45) attains nearly the ratio of quartz as supported by XPS. The OH absorption found in the spectra is related mostly to the hydroxyl group in the case of films from HMDSO and associated with a water contamination in the OMCTS film.

The better radial homogeneity, lower C content, the higher cross-linking of $SiO_x$ films and the characteristic absorption of the LO-TO pair in the ATR-FTIR spectra signify a promising potential of the films from OMCTS regarding the deposition of scratch resistant films on polymer surfaces.

## 5. References

[1] M. Laroussi, T. Akan, Plasma Process. Polym. 2007, 4, 777
[2] R. Foest, E. Kindel, A. Ohl, M. Stieber, K.-D. Weltmann, Plasma Phys. Contr. Fusion 47 (2005) B525-B536
[3] J. Schäfer, R. Foest, A. Quade, A. Ohl, K.-D. Weltmann, J. Phys. D: Appl. Phys. 41 (2008)
[4] L. Zajickova, J. Janca, V. Perina, Thin Solid Films 338 (1999) 45-59
[5] J. Benedikt, K. Focke, A. Yanuas-Gil, A. v. Keudell, Appl. Phys. Let. 89, 251504 (2006)
[6] Y. Qi, Z. G. Xiao, T. D. Mantei, J. Vac. Sci. Technol. A 21(4), (2003)
[7] W. Bensch, W. Bergholz, Semicond. Sci. Technol. 5 (1990) 421-428