Correlation between chemical structure and functional properties of organosilicon plasma polymers and SiO_2-like films

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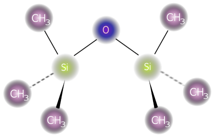
Outline

Motivation

Hexamethyldisiloxane (HMDSO)
- versatile starting material for PECVD:

- source of Si-O-Si bonds (especially for $HMDSO/O_2$)
- source of Si-C bonds

HMDSO



PECVD in low pressure rf capacitively coupled discharges (CCP)
- variety of different materials can be prepared when using the mixture of $HMDSO/O_2$ in varying deposition conditions:

- percentage of HMDSO in $HMDSO/O_2$
- pressure p
- rf power P
- dc self-bias U_b (in relation with P and p)

How these materials react to annealing?

PECVD using HMDSO at atmospheric pressure: competition with low pressure process in achievement of silica-hard coatings
Will help an increased deposition temperature?

PECVD in low pressure rf CCP from HMDSO/O_2

- frequency of 13.56 MHz
- capacitive ac coupling
- asymmetric arrangement

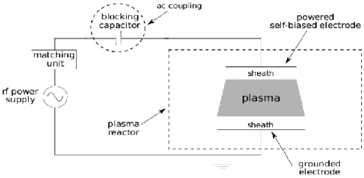
$$\xi = \frac{A_{\mathrm{rf}}}{A_{\mathrm{g}}} \approx 0.6$$

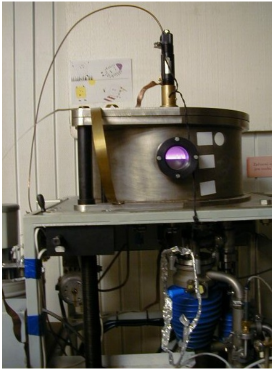
$$U_{\mathrm{b}} = 0.83\, V_{\mathrm{rf}} \frac{\xi^q - 1}{\xi^q + 1}, \quad q = 1.25 - 4$$

for

$$q = 2.5 \Longrightarrow \xi = -0.55$$

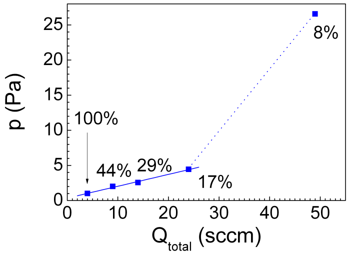
- $c_{\mathrm{hmdso}} = 5$–$100\,\%$
- $p = 1$–40 Pa
- $P = 100$–450 W
- $U_{\mathrm{b}} =$ from -20 to -335 V



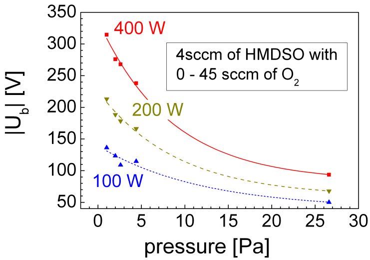


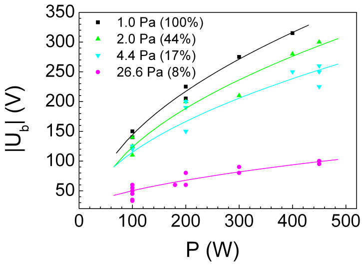
Relation between power, self-bias and pressure

variation of HMDSO % in the mixture $\Longleftrightarrow$ variation of Q_{O2} at the fixed $Q_{HMDSO} = 4$ sccm

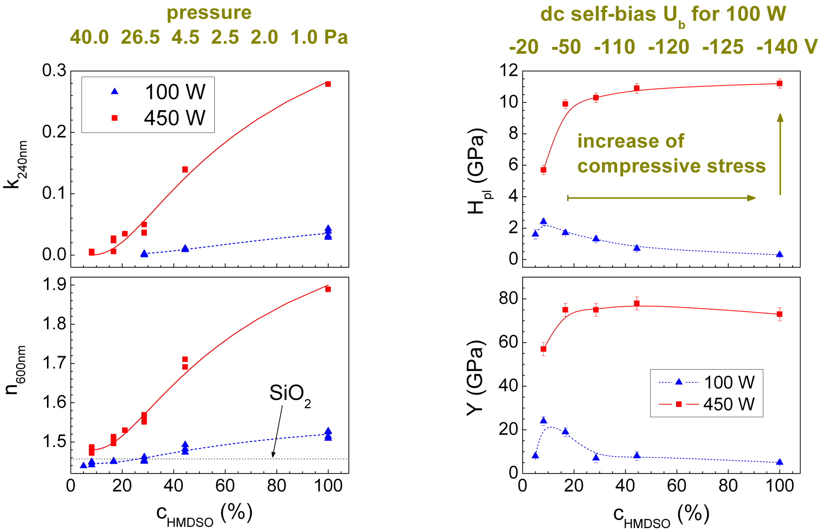


decrease of HMDSO % $\Longrightarrow$ increase of pressure (expecially for 5–8 %)
$\Longrightarrow$ decrease of ion energy flux





Mechanical and optical properties



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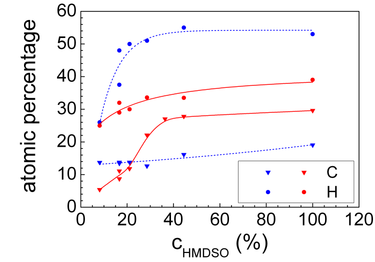
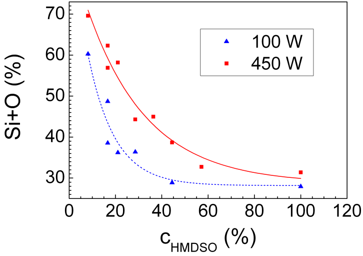
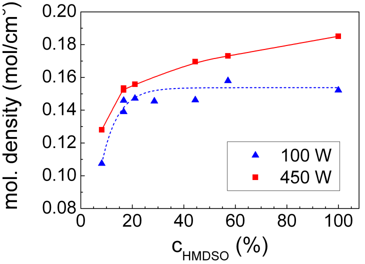
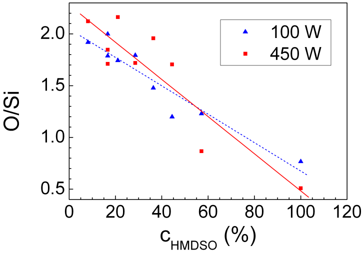
Composition and density









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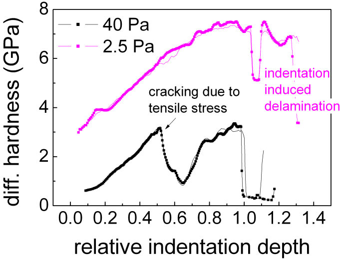
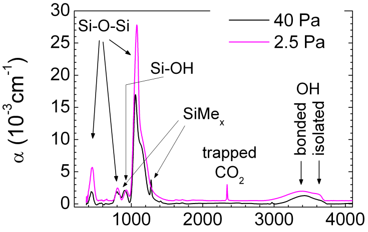
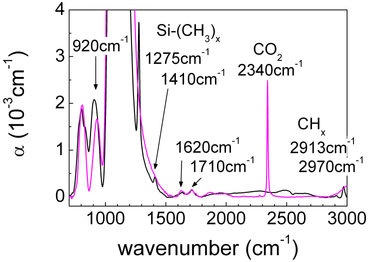
5 % HMDSO, effect of pressure

p (Pa)	Q_{HMDSO} (sccm)	Q_{O2} (sccm)	P (W)	U_b (V)
40	4	80	100	-20
2.5	0.7	14	100	-120

Si (%)	O (%)	C (%)	H (%)
25	43	10	22
23	56	1	20





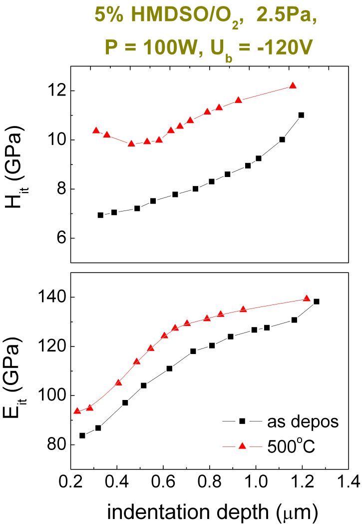


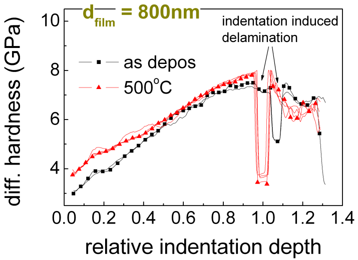
p (Pa)	H_{IT} (GPa)	E_{IT} (GPa)
40	1.6 ± 0.3	8 ± 1
2.5	6.9 ± 0.5	63 ± 4

Temperature Induced Changes

- Annealing induced changes in SiO_2-like films deposited in low pressure (2.5 Pa) CCP from 5 % HMDSO/O_2
- Improvement of mechanical properties of SiO_2-like films deposited in atmospheric pressure dielectric barrier discharge (DBD) by slight increase of deposition temperature
- Improvement of mechanical properties of $SiO_xC_yH_z$ film deposited in CCP from 8 % HMDSO/O_2 at 450 W by annealing
- Annealing experiments for the films deposited in CCP from HMDSO-rich mixtures (17, 44 and 100 % of HMDSO)

5 % HMDSO, 2.5 Pa / SiO_2-like film in CCP





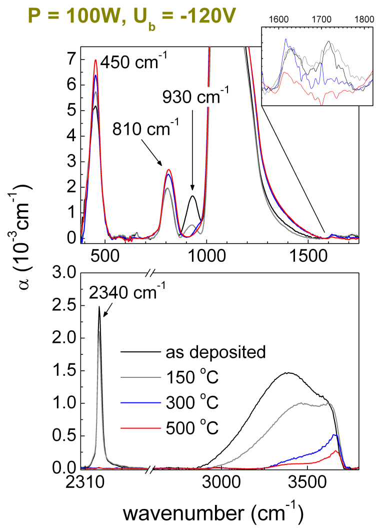
Originally:

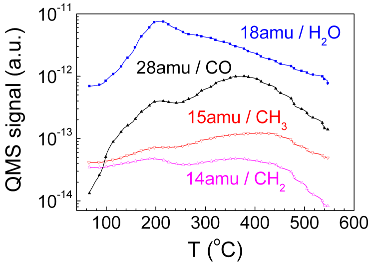
- compressively stressed film with good fracture toughness

Annealing:

- slight stress relaxation due to annealing
- decrease of hardness induced by stress relaxation compensated by creation of new Si-O-Si bonds instead of Si-OH

5 % HMDSO, 2.5 Pa / SiO_2-like film in CCP

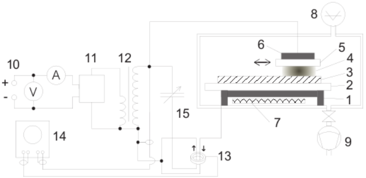




As deposited film:

- Si 23 %, O 56 %, C 1 %, H 20 %

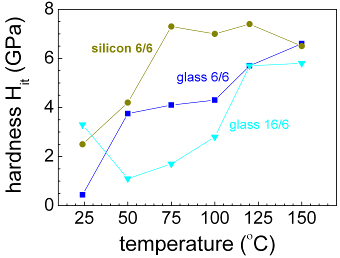
SiO_2-like films in atmospheric pressure DBD

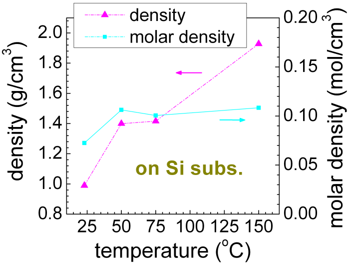


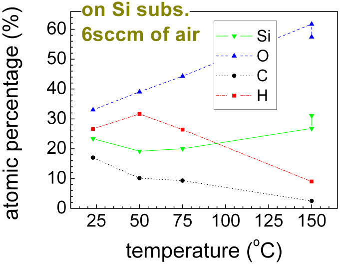
- Townsend-like (homogeneous) discharge at 6 kHz
- max. power 10 W/cm^3
- discharge gap of 0.5 mm
- upper electrode covered by Simax (1.5 mm thick)
- bottom covered by glass substrate or glass plate (1mm thick) with Si substrate
- substrate temperature 23–150 °C

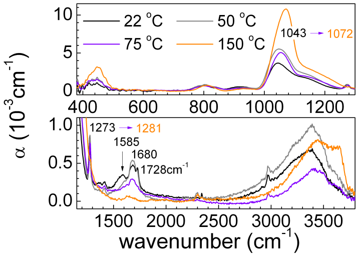
- HMDSO / synthetic air / nitrogen
- 6 sccm of N_2
- 6 slm of synthetic air
- 6 or 16 sccm of air through liquid HMDSO
  - 6 sccm ⇒ 70 ppm of HMDSO, 200 ppm of O_2 in N_2
  - 16 sccm ⇒ 173 ppm of HMDSO, 532 ppm of O_2 in N_2

SiO_2-like films in atmospheric pressure DBD









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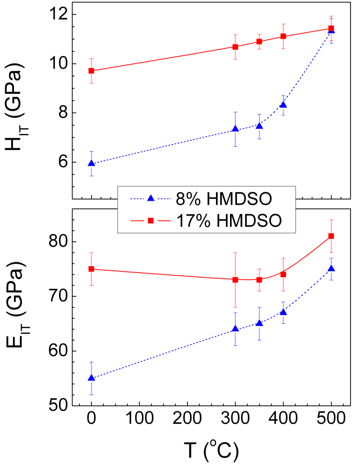
CCP 450 W, 8 and 17 % HMDSO

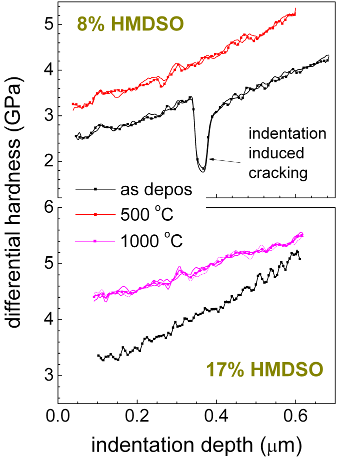
Critical depth for indentation induced crack initiation in μm:

% / T (°C)	–	300	350	400	500
8	0.34	0.42	0.44	0.45	> 1
17	> 1	> 1	> 1	> 1	0.46

8% HMDSO: p = 26.5Pa, U_b = -100V

17% HMDSO: p = 4.5Pa, U_b = -250V

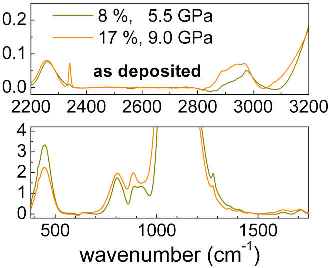


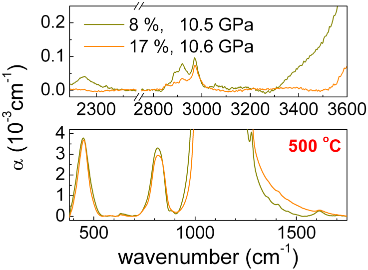


CCP 450 W, 8 and 17 % HMDSO

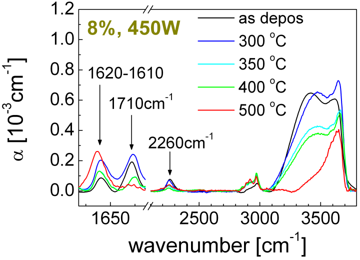
as deposited:

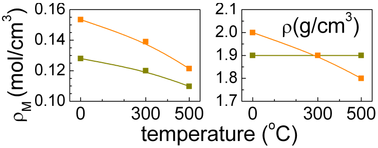
%	8 %	17 %
Si	22	20
O	47	37
C	5	11
H	25	32



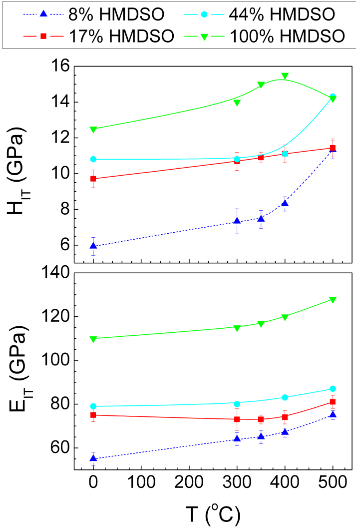


% HMDSO	T (°C)	O/Si	H/Si	C/Si
8	-	2.12	1.12	0.24
8	300	1.94	0.81	0.29
8	500	1.93	0.55	0.21
17	-	1.85	1.60	0.56
17	300	1.79	1.37	0.57
17	500	1.99	1.01	0.57

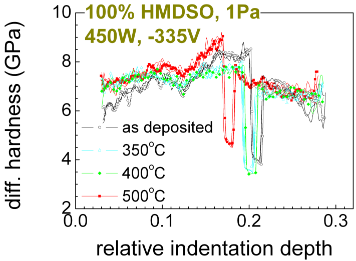




CCP 450 W, 44 and 100 % HMDSO



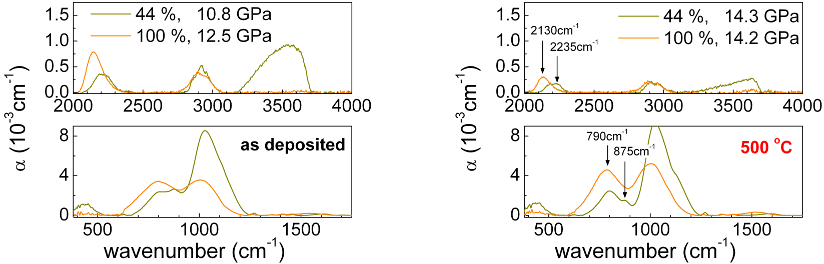
c_{hmdso} (%)	8	17	44	100
p (Pa)	26.5	4.5	2	1
U_{b} (V)	-100	-250	-300	-335



- 100 and 44 % films are compressively stressed but the hardness does not decreases with annealing temperature
- fracture toughness is not as good as for 8 and 17 % films and does not improve with annealing

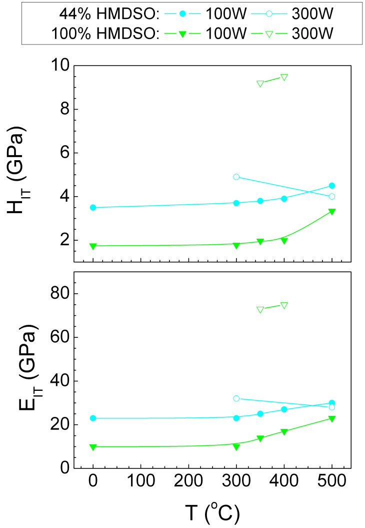
CCP 450 W, 44 and 100 % HMDSO

c_{hmdso}	T (°C)	Si (%)	O (%)	C (%)	H (%)	O/Si	C/Si	H/Si
44 %	–	15	18	28	39	1.2	1.9	2.6
44 %	500	14	20	31	35	1.4	2.2	2.5
100 %	–	17	9	32	42	0.5	1.9	2.5
100 %	500	20	7	39	34	0.4	2.0	1.7



c_{hmdso}	T (°C)	ϱ (g/cm^3)	ϱ_{M} (mol/cm^3)
44 %	–	1.8	0.17
44 %	500	1.8	0.16
100 %	–	1.8	0.17
100 %	500	1.8	0.15

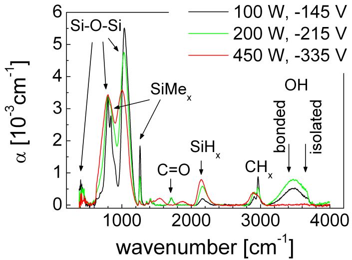
CCP 100 and 300 W, 44 and 100 % HMDSO



Self-bias U_b for 44 and 100 % HMDSO/O_2 (2 and 1 Pa) at different rf powers:

P (W) / c_{hmdso} (%)	44	100
100	-120	-145
300	-230	-270
450	-300	-335

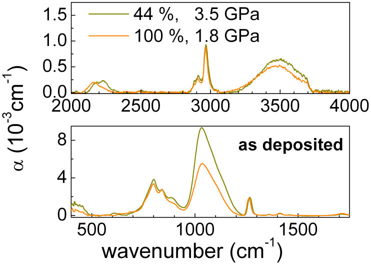
- 100 % HMDSO film is soft polymeric material which hardness can be slightly increased by annealing and significantly improved by increased rf power.

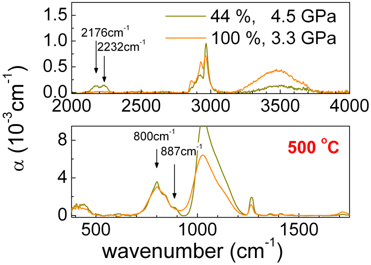


- Films deposited at 300 W were not stable ⟹ peeled off when not annealed

CCP 100 W, 44 and 100 % HMDSO

c_{hmdso}	T (°C)	Si (%)	O (%)	C (%)	H (%)	O/Si	C/Si	H/Si
44 %	–	15	20	17	48	1.3	1.1	3.2
44 %	500	15	25	20	40	1.7	1.3	2.7
100 %	–	12	18	21	49	1.5	1.8	4.1
100 %	500	12	19	22	47	1.6	1.8	3.9





c_{hmdso}	T (°C)	ϱ (g/cm^3)	ϱ_{M} (mol/cm^3)
44 %	–	1.4	0.14
44 %	500	1.4	0.12
100 %	–	1.2	0.13
100 %	500	1.3	0.14

Conclusion

- Understanding of the changes in film mechanical properties (because of different deposition parameters or annealing) requires complete study of the film composition, chemical bonds and film density. Thermal desorption spectroscopy is advantageous.
- Molar density increased with increased deposition temperature of APTD films and decreased with annealing temperature of CCP films.
- Significant hydrocarbon desorption observed only for increased deposition temperature of APTD-$SiO_xC_yH_z$ films.
- For CCP films, carbon desorption detected only for annealing of SiO_2-like film (5 % HMDSO, 2.5 Pa) - rather decrease of CO_2 than CH_x. Desorption of -OH and -H more important.
- Annealing of compressively stressed CCP films led to their stabilization due to stress relaxation.
- Annealing of hard compressively stressed films (either SiO_x:H or $SiO_xC_yH_z$) did not decrease but increase the hardness - stress relaxation is compensated by cross-linking of material, i.e. replacing the end-groups (Si-OH, Si-H, C=O) by new strong bonds.