

3. Experimental

3.1. Substrates and chemicals used in plasma polymerization

Silicon wafers cut to $\sim 1.0 \times 1.0 \text{ cm}^2$ were used as substrates for the plasma polymer deposition. These substrates were placed in iso-propanol in an ultrasonic bath for 5 min. This was followed by rinsing with acetone for 5 min again in the ultrasonic bath. Finally, the substrates were allowed to dry in air. Samples were stored in clean aluminum foils prior to use. Just, before insertion in the plasma chamber all substrates were again rinsed in acetone.

Liquid styrene (CAS 100-42-5), allyl alcohol (CAS 107-18-6), and allylamine (CAS 107-11-9) with 99 % purity or higher were purchased from Merck Chemie GmbH, Germany. Argon, purity > 99%, and ethylene, purity > 99.9% was supplied from Messer-Griessheim AG, Germany.

Polystyrene oligomer powders with a molecular weight of 3420 g/mol were obtained from Polymer Standard Service, Germany. Low density polyethylene powder was obtained from Goodfellow GmbH, Germany. Poly(allylamine) solution (20 wt % in water) with a molecular weight of 17000 g/mol was obtained from Sigma Aldrich Chemie GmbH, Germany.

3.2. Preparation of conventional polymer films

Polystyrene (PS-R) and polyethylene (PE-R) reference samples were prepared by coating Si substrates with 3 wt % solutions of styrene and ethylene in toluene, respectively. Poly(allylamine) reference sample (PAAmin-R) was prepared by depositing the 20 wt % poly(allylamine) solution in water onto a silicon substrate.

3.3. Plasma deposition equipment

The scheme of the stainless steel plasma reaction chamber is presented in Figure 3.1. The chamber was mounted on sample transfer chamber of the ToF-SIMS instrument. In that way the samples prepared could be directly transferred to the sample analysis chamber of ToF-SIMS instrument without any exposure to air. The plasma chamber is a cylindrical reactor with an internal diameter of 20 cm and a length of 20 cm. The substrate is kept in between two parallel plate electrodes ($2 \times 2 \text{ cm}^2$) separated by a distance of 5 cm, one grounded and the other used as the power electrode. The chamber was pumped down

to a base pressure of 10^{-4} Pa by a turbo pump. During the reaction, a baratron gauge (Type 626, MKS, Munich, Germany) is used to measure the pressure inside the plasma chamber.

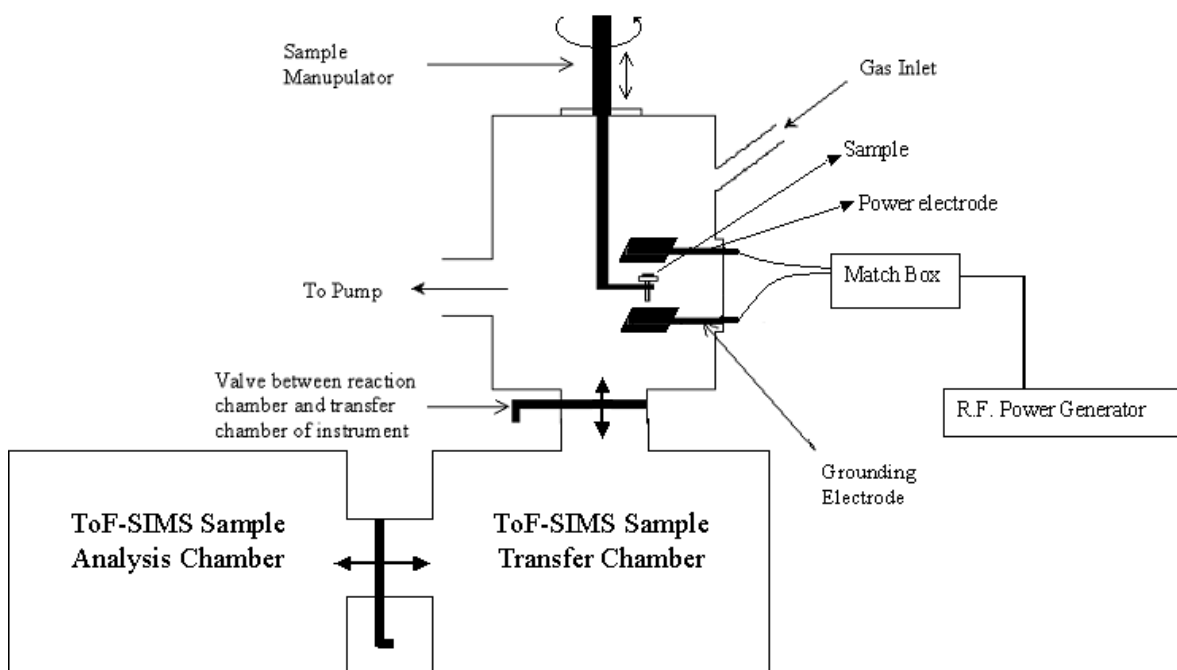


Figure 3.1. Schematic drawing of plasma chamber.

A r.f. plasma generator combined with a matching unit (CESARTM 136 Generator with VM1500, Dressler, Stolberg, Germany) was used to establish the plasma in the reactor. The generator was used with 13.65 MHz r.f. The pulse frequency could be chosen in a range between 10 and 10^4 Hz and the duty cycle value of the pulses was variable between 0.01 and 0.90. The power could be adjusted in a range between 1 and 650 W.

Before each deposition involving a new monomer the apparatus was cleaned with iso-propanol and acetone and then air-dried.

3.4. Preparation of plasma polymer films

3.4.1. Procedure applied for plasma polymerization

The silicon substrate is kept in the middle of the parallel plate electrodes. Before plasma polymerization, the substrate is cleaned with Argon plasma for 5 min at a pressure of 5.0 Pa, plasma power of 10 W (continuous mode) and with a gas flow rate of 10 sccm.

The monomer is introduced into the plasma chamber at a desired flow rate and the reaction pressure is set to a desired value. For all deposition processes the pulse frequency

was kept at 1 kHz. After setting the duty cycle value, the RF generator is switched on. The deposition time was adjusted to produce a film thickness of ca. 50 nm. No substrate related secondary ion signals contributed to the SSIMS spectra. Upon completion of deposition, the RF source was switched off, the monomer flow was cut off, and the reactor evacuated back to its original base pressure for at least 5 min in order to remove excess monomer vapor. Finally, deposited plasma polymers were transferred to the analysis chamber of ToF-SSIMS instrument for analysis.

3.4.2. Preparation of plasma deposited styrene films (PDS)

Liquid styrene was kept at 60 °C in a round bottom flask, which was connected to the plasma chamber by a heated stainless steel gas-pipe. A dosing valve permitted to keep the pressure of the styrene vapor in the plasma chamber at a desired level. To check the effect of external plasma parameters on the chemistry of deposited films, styrene was polymerized at varying power and duty cycle (see Table 3.1 for conditions of deposition and corresponding plasma on and off times for described duty cycle values).

Table 3.1. Plasma deposited polystyrene films and external plasma parameters employed for their deposition.

Sample	Plasma Power (W)	Duty Cycle	Plasma on time (ms)	Plasma off time (ms)	Pressure (Pa)	Varied parameter
PDS-1	10.0	0.1	0.1	0.9	5.0	Duty cycle
PDS-2	10.0	0.33	0.33	0.67	5.0	
PDS-3	10.0	0.70	0.7	0.3	5.0	
PDS-4	10.0	CW	1.0	0.0	5.0	
PDS-4	10.0	CW	1.0	0.0	5.0	Power in CW mode
PDS-5	20.0	1.0 (CW)	1.0	0.0	5.0	
PDS-6	30.0	1.0 (CW)	1.0	0.0	5.0	
PDS-7	40.0	1.0 (CW)	1.0	0.0	5.0	
PDS-8	60.0	1.0 (CW)	1.0	0.0	5.0	

3.4.3. Preparation of plasma deposited ethylene films (PDE)

The plasma polymerization of ethylene was carried out at a constant monomer flow, which was adjusted by a gas flow controller (MKS, München, Germany). Ethylene was polymerized at varying plasma power, monomer pressure in reactor, flow rate of the monomer and duty cycle (c.f. Table 3.2).

Table 3.2. Plasma polymerized ethylene films (PDE) and external plasma parameters employed for their deposition.

Sample	Plasma Power (W)	Pressure (Pa)	Flow rate (sccm)	Duty cycle	Plasma on time (ms)	Plasma off time (ms)	Varied parameter
PDE-1	20	5.1	20	0.05	0.05	0.95	Duty cycle
PDE-2	20	5.1	20	0.1	0.1	0.9	
PDE-3	20	5.1	20	0.25	0.25	0.75	
PDE-4	20	5.1	20	0.5	0.5	0.5	
PDE-5	20	5.1	20	1.0 (CW)	1.0	0.0	
PDE-6	10	5.1	20	0.1	0.1	0.9	Plasma power in pulsed mode
PDE-2	20	5.1	20	0.1	0.1	0.9	
PDE-7	30	5.1	20	0.1	0.1	0.9	
PDE-8	50	5.1	20	0.1	0.1	0.9	
PDE-9	100	5.1	20	0.1	0.1	0.9	
PDE-10	10	5.1	20	1.0 (CW)	1.0	0.0	Plasma power in CW mode
PDE-5	20	5.1	20	1.0 (CW)	1.0	0.0	
PDE-11	50	5.1	20	1.0 (CW)	1.0	0.0	
PDE-12	20	5.1	10	0.1	0.1	0.9	Flow rate
PDE-2	20	5.1	20	0.1	0.1	0.9	
PDE-13	20	5.1	30	0.1	0.1	0.9	
PDE-14	20	5.1	40	0.1	0.1	0.9	
PDE-15	20	2.0	20	0.1	0.1	0.9	Reaction Pressure
PDE-16	20	3.5	20	0.1	0.1	0.9	
PDE-2	20	5.1	20	0.1	0.1	0.9	

3.4.4. Preparation of plasma deposited allylamine (PDA Amin) and plasma deposited allyl alcohol films (PDA Al)

During deposition of the plasma polymers, the reaction pressure in the plasma chamber was kept at 5.1 Pa. Plasma polymers were deposited at different duty cycles, plasma powers and monomer flow rates. Flow rates of the monomers were adjusted by a liquid flow controller (MÄTTIG, Germany). Table 3.3 and Table 3.4 summarize the deposition conditions for allylamine and alcohol plasma polymers, respectively.

Table 3.3. Plasma polymerized allylamine films (PDA Amin) and external plasma parameters employed for their deposition.

Sample	Plasma Power (W)	Flow rate (sccm)	Duty cycle	Plasma on time (ms)	Plasma off time (ms)	Varied parameter
PDA Amin-1	20	20	0.05	0.05	0.95	Duty cycle
PDA Amin-2	20	20	0.1	0.1	0.9	
PDA Amin-3	20	20	0.25	0.25	0.75	
PDA Amin-4	20	20	0.5	0.5	0.5	
PDA Amin-5	20	20	1.0 (CW)	1.0	0.0	
PDA Amin-6	10	20	1.0 (CW)	1.0	0.0	Plasma power in CW mode
PDA Amin-5	20	20	1.0 (CW)	1.0	0.0	
PDA Amin-7	30	20	1.0 (CW)	1.0	0.0	
PDA Amin-8	40	20	1.0 (CW)	1.0	0.0	
PDA Amin-9	50	20	1.0	1.0	0.0	
PDA Amin-10	20	2	0.1	0.1	0.9	Flow rate
PDA Amin-11	20	10	0.1	0.1	0.9	
PDA Amin-2	20	20	0.1	0.1	0.9	

Table 3.4. Plasma polymerized allyl alcohol films (PDAAI) and external plasma parameters employed for their deposition.

Sample	Plasma Power (W)	Flow rate (sccm)	Duty cycle	Plasma on time (ms)	Plasma off time (ms)	Varied parameter
PDAAI-1	20	20	0.05	0.05	0.95	Duty cycle
PDAAI-2	20	20	0.1	0.1	0.9	
PDAAI-3	20	20	0.25	0.25	0.75	
PDAAI-4	20	20	0.5	0.5	0.5	
PDAAI-5	20	20	1.0	1.0	0.0	
PDAAI-5	20	20	1.0 (CW)	1.0	0.0	Plasma Power in CW mode
PDAAI-6	50	20	1.0 (CW)	1.0	0.0	
PDAAI-7	20	2	0.1	0.1	0.9	Flow rate
PDAAI-8	20	10	0.1	0.1	0.9	
PDAAI-2	20	20	0.1	0.1	0.9	

3.4.5. Preparation of plasma copolymer films

Two monomers were introduced via a T-piece to ensure an adequate mixing of the vapors before they reached the glow region of the plasma. The flow rate of each monomer was adjusted separately. The total flow rate was kept constant but the partial flow rates of the monomer were varied to prepare plasma copolymers at different feed gas compositions. All other external plasma parameters were kept constant. Table 3.5 summarizes the deposition conditions employed for plasma copolymerization.

Table 3.5. Plasma polymerized copolymer films and external plasma parameters employed for their deposition.

Sample	1. monomer	2. monomer	% of 1. monomer	% of 2. monomer	Other external plasma parameters
PDE-AAI-1	Ethylene	Allyl alcohol	100	0	20 W, d.c. = 0.1 5.0 Pa, 20 sccm
PDE-AAI-2			75	25	
PDE-AAI-3			62.5	37.5	
PDE-AAI-4			50	50	
PDE-AAI-5			37.5	62.5	
PDE-AAI-6			25	75	
PDE-AAI-7			0	100	
PDS-AAI-1	Styrene	Allyl alcohol	100	0	20 W, d.c. = 0.5 5.0 Pa, 13 sccm
PDS-AAI-2			80	20	
PDS-AAI-3			60	40	
PDS-AAI-4			50	50	
PDS-AAI-5			40	60	
PDS-AAI-6			20	80	
PDS-AAI-7			0	100	
PDE-AAmin-1	Ethylene	Allylamine	100	0	20 W, d.c. = 0.1 5.0 Pa, 20 sccm
PDE-AAmin-2			85	15	
PDE-AAmin-3			60	40	
PDE-AAmin-4			50	50	
PDE-AAmin-5			40	60	
PDE-AAmin-6			20	80	
PDE-AAmin-7			0	100	
PDS-AAmin-1	Styrene	Allylamine	100	0	20 W, d.c. = 0.5 5.0 Pa, 13 sccm
PDS-AAmin-2			80	20	
PDS-AAmin-3			60	40	
PDS-AAmin-4			50	50	
PDS-AAmin-5			40	60	
PDS-AAmin-6			20	80	
PDS-AAmin-7			0	100	

