3. Experimental

3.1. Substrates and chemicals used in plasma polymer deposition

Silicon wafers cut to approximately 1cm by 1cm square pieces were used as substrates for the plasma polymer deposition. These substrates were cleaned first by iso-propanol followed by acetone in an ultrasonic bath for 5 minutes each. The substrates were allowed to dry and then stored in clean aluminum foils prior to use.

Liquid styrene (CAS 100-42-5), allyl alcohol (CAS 107-18-6), and allyl amine (CAS 107-11-9) with at least 99 % purity were purchased from Merck Chemie GmbH, Germany. Argon, purity > 99 %, and ethylene, purity > 99.9 % was supplied from Messer-Griessheim AG, Germany and were used without purification. Polystyrene oligomer powders of molecular weight 3420g.mol^{-1} were obtained from Polymer Standard Service, Germany. Low density polyethylene powder was obtained from Goodfellow GmbH, Germany.

3.2. Preparation of reference polymer films

Polystyrene (PS-refer) and polyethylene (PE) reference samples were prepared by coating Si substrates with 3 wt% solutions of polystyrene and polyethylene in toluene.

3.3. Plasma deposition equipment

Figure 3.1 shows the scheme of the plasma deposition chamber. This chamber could be mounted on the XPS as well as NEXAFS experiments so that the samples prepared in the chamber can be transferred for analysis without exposure to air. The chamber is cylindrical with an internal diameter of 20 cm and a length of 20 cm. The parallel plate electrodes of 2 cm by 2 cm each are separated by a distance of 5 cm. The substrate is placed between these two parallel plate electrodes. One of these electrodes is grounded while the other is used as the power electrode. The chamber is pumped down to a base pressure of 10^{-4} Pa by a turbo pump. A baratron gauge (Type 626, MKS, Munich, Germany) is used to measure the pressure inside the chamber during the experiment. An r.f. generator combined with a matching unit (CESAR with VM1500, Dressler, Stolberg, Germany) were used to establish the plasma in the reactor. The generator was operated at 13.56 MHz r.f. frequency. The pulse frequency can be chosen in a wide range between 10 to 10^4 Hz and the duty cycle of the pulses is variable between 0.01 and 0.9. The power can be adjusted between a range of 1 and 650 W.

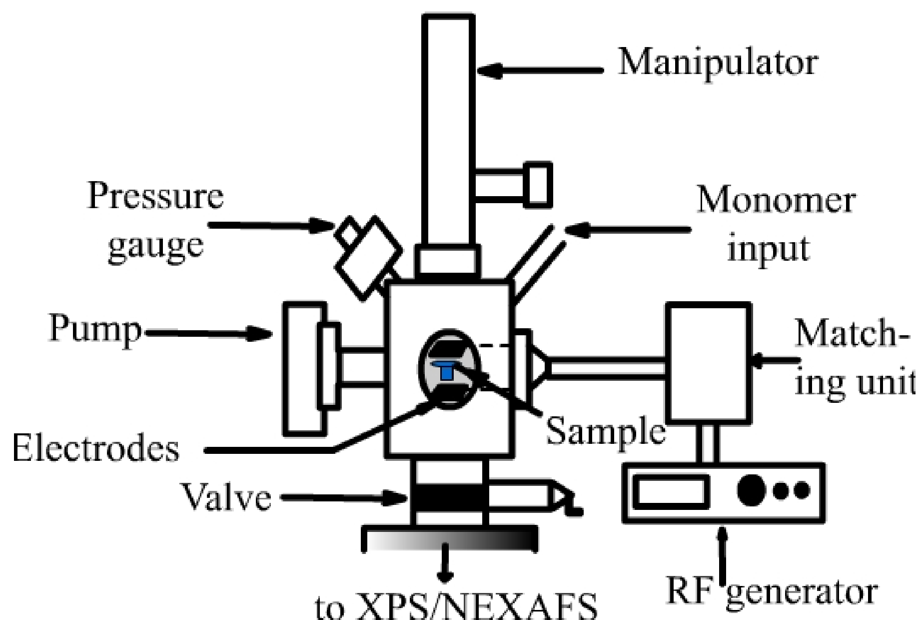

Figure 3.1: Schematic representation of the plasma deposition chamber

3.4. Preparation of plasma polymer films

3.4.1. General procedure for plasma polymerization

Before introducing the monomer for polymerization each silicon substrate is cleaned in an argon plasma in the deposition chamber for 5 minutes at a pressure of 5 Pa, power of 10 W in continuous mode and with a flow rate of 10 sccm. The monomer was then introduced into the plasma chamber at a desired flow rate and the desired reaction pressure was achieved. The pulse frequency in each case was 1000 Hz. The duty cycle was set before the RF generator was switched on. Films of sufficient thickness (approximately 50-100 nm) were obtained. The generator and later the monomer supply was switched off and the deposition chamber was evacuated back to its base pressure. The prepared sample was then transferred to the analysis chamber of the XPS or NEXAFS spectrometer.

3.4.2. Preparation of plasma deposited ethylene

Plasma deposited ethylene films were obtained at varying duty cycle, power and reaction pressure. The monomer flow rate was kept constant using a gas flow controller (MKS, Munich, Germany). Two different sets of samples were prepared, one set for XPS analysis while another set for NEXAFS analysis (Table 3.1).

3.4.3. Preparation of plasma deposited styrene films

Plasma deposited styrene films were obtained at varying external plasma parameters. Two different sets of experiments were performed for XPS and NEXAFS studies (Table 3.2). Vapor of the styrene monomer was introduced into the deposition chamber through a heated stainless steel tube connected to a round bottom flask containing styrene at 60°C. A dosing valve was used to control the vapor flow to the deposition chamber and to keep the reaction pressure constant at the desired level.

3.4.4. Preparation of plasma deposited allyl alcohol and allylamine films

The flow of allyl alcohol or allyl amine into the deposition chamber was controlled using a liquid flow controller (MÄTTIG, Germany). The films were prepared at different duty cycle, power and pressure. Again two sets of experiments were performed for each monomer, one set for the XPS studies and another set for the NEXAFS studies. Details of these experiments are given in Table 3.3 and 3.4.

3.4.5. Preparation of plasma deposited copolymer films

Plasma deposited copolymer films were prepared by introducing two different monomers in the plasma chamber through a T-piece to ensure an adequate mixing of the vapors before they reach 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 monomers 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.

3.5. Aging Studies

After the analysis of samples by XPS and NEXAFS without exposure to air the samples were exposed to ambient air and were stored in Fluoro-ware wafer trays. The samples were stored at room temperature in darkness and were removed for analysis at different intervals of exposure time. Special care was taken to avoid the contact of the film surface with any other surface while storage or during preparation for analysis.

Table 3.1: Experimental details of plasma deposited ethylene films and external plasma parameters employed for their deposition during XPS and NEXAFS studies.

Experiment	XPS			NEXAFS		
Duty cycle variation	Duty cycle	Sample names	Fixed parameters	Duty cycle	Sample names	Fixed parameters
	0.1 0.25 0.5 1.0	X-PDE1 X-PDE2 X-PDE3 X-PDE4	20 W, 5 Pa, 20 sccm, Pulse time period=1ms	0.1 0.7 1.0	N-PDE1 N-PDE2 N-PDE3	10 W, 5 Pa 20 sccm, Pulse time period=1ms
Power variation	Power (W)	Sample names	Fixed parameters	Power (W)	Sample names	Fixed parameters
	20 30 50 100	X-PDE1 X-PDE5 X-PDE6 X-PDE7	0.1, 5 Pa, 20 sccm, Pulse time period=1ms	5 10 20 30	N-PDE4 N-PDE1 N-PDE5 N-PDE6	0.1, 5 Pa, 20 sccm, Pulse time period=1ms
Pressure variation	Pressure (Pa)	Sample names	Fixed parameters	Pressure (Pa)	Sample names	Fixed Parameters
	2 3.5 7.5 15	X-PDE8 X-PDE9 X-PDE10 X-PDE11	0.1, 20W, 20 sccm, Pulse time period=1ms	5 16 24 32	N-PDE1 N-PDE7 N-PDE8 N-PDE9	0.1, 10 W, 20 sccm, Pulse time period=1ms

Table 3.2: Experimental details of plasma deposited styrene films and external plasma parameters employed for their deposition during XPS and NEXAFS studies.

Experiment	XPS			NEXAFS		
Duty cycle variation	Duty cycle	Sample names	Fixed parameters	Duty cycle	Sample names	Fixed parameters
	0.02 0.1 0.25 0.5 1.0	X-PDS1 X-PDS2 X-PDS3 X-PDS4 X-PDS5	20 W, 5 Pa, Pulse time period=1ms	0.05 0.1 0.25 0.5 1.0	N-PDS1 N-PDS2 N-PDS3 N-PDS4 N-PDS5	20 W, 5 Pa Pulse time period=1ms
Power variation	Power (W)	Sample names	Fixed parameters	Power (W)	Sample names	Fixed parameters
	20 50	X-PDS5 X-PDS6	1, 5 Pa	20 30 50	N-PDS5 N-PDS6 N-PDS7	1, 5 Pa
Pressure variation	Pressure (Pa)	Sample names	Fixed parameters	Pressure (Pa)	Sample names	Fixed Parameters
	2 8	X-PDS7 X-PDS8	0.6, 40 W, Pulse time period=1ms	2 5 10	N-PDS8 N-PDS2 N-PDS9	0.1, 20 W, Pulse time period=1ms

Table 3.3: Experimental details of Plasma deposited allyl alcohol films and external plasma parameters employed for their deposition during XPS and NEXAFS studies.

Experiment	XPS			NEXAFS		
	Duty cycle	Sample names	Fixed parameters	Duty cycle	Sample names	Fixed parameters
Duty cycle variation	0.05 0.1 0.5 1.0	X-PDA2 X-PDA3 X-PDA4 X-PDA5	20 W, 5 Pa, 20 sccm, Pulse time period=1ms	0.02 0.1 0.5 1.0	N-PDA1 N-PDA2 N-PDA3 N-PDA4	20 W, 5 Pa, 20 sccm, Pulse time period=1ms
	Power (W)	Sample names	Fixed parameters	Power (W)	Sample names	Fixed parameters
Power variation	5 20 30	X-PDA1 X-PDA3 X-PDA6	0.1, 5 Pa, 20 sccm, Pulse time period=1ms	20 50	N-PDA3 N-PDA5	0.5, 5 Pa, 20 sccm, Pulse time period=1ms
	Pressure (Pa)	Sample names	Fixed parameters	Pressure (Pa)	Sample names	Fixed Parameters
Pressure variation	2 5 7	X-PDA1 X-PDA3 X-PDA6	0.1, 20 W, 20 sccm, Pulse time period=1ms	2 5	N-PDA2 N-PDA6	0.1, 20 W, 20 sccm, Pulse time period=1ms

Table 3.4: Experimental details of Plasma deposited allylamine films and external plasma parameters employed for their deposition during XPS and NEXAFS studies.

Experiment	XPS			NEXAFS		
	Duty cycle	Sample names	Fixed parameters	Duty cycle	Sample names	Fixed parameters
Duty cycle variation	0.05 0.1 0.5 1.0	X-PDAm1 X-PDAm2 X-PDAm3 X-PDAm4	20 W, 5 Pa, 20 sccm, Pulse time period=1ms	0.1 0.5 0.7 1.0	N-PDAm1 N-PDAm2 N-PDAm3 N-PDAm4	20 W, 5 Pa, 20 sccm, Pulse time period=1ms
	Power (W)	Sample names	Fixed parameters	Power (W)	Sample names	Fixed parameters
Power variation	20 30 50	X-PDAm4 X-PDAm5 X-PDAm6	1.0, 5 Pa, 20 sccm	10 20 40 50	N-PDAm5 N-PDAm4 N-PDAm6 N-PDAm7	1.0, 5 Pa, 20 sccm
	Pressure (Pa)	Sample names	Fixed parameters	Pressure (Pa)	Sample names	Fixed Parameters
Pressure variation	2 5 15	X-PDAm7 X-PDAm2 X-PDAm8	0.1, 20 W, 20 sccm, Pulse time period=1ms	5 15	N-PDAm2 N-PDAm8	0.5, 20 W, 20 sccm, Pulse time period=1ms

Table 3.5: Experimental details of plasma deposited copolymer films and external plasma parameters employed for their deposition during XPS and NEXAFS studies.

1st monomer	2nd monomer	% Partial flow rate of 1st monomer	% Partial flow rate of 2nd monomer	XPS samples	NEXAFS samples	Other external plasma parameters
Ethylene	Allyl alcohol	100	0	X-Etal1	N-Etal1	20 W, 0.1, 5 Pa, 20 sccm, Pulse time period= 1ms
		90	10	X-Etal2	N-Etal2	
		70	30	X-Etal3	N-Etal3	
		30	70	X-Etal4	N-Etal4	
		10	90	X-Etal5	N-Etal5	
		0	100	X-Etal6	N-Etal6	
Styrene	Allyl alcohol	100	0	X-Stal1	N-Stal1	20 W, 0.1, 5 Pa, 20 sccm, Pulse time period= 1ms
		90	10	X-Stal2	N-Stal2	
		50	50	X-Stal3	N-Stal3	
		10	90	X-Stal4	N-Stal4	
		0	100	X-Stal5	N-Stal5	
Ethylene	Allylamine	100	0	X-Etam1	N-Etam1	20 W, 0.1, 5 Pa, 20 sccm, Pulse time period= 1ms
		70	30	X-Etam2	N-Etam2	
		50	50	X-Etam3	N-Etam3	
		30	70	X-Etam4	N-Etam4	
		0	100	X-Etam5	N-Etam5	
Styrene	Allylamine	100	0	X-Stam1	N-Stam1	20 W, 0.1, 5 Pa, 20 sccm, Pulse time period= 1ms
		90	10	X-Stam2	N-Stam2	
		70	30	X-Stam3	N-Stam3	
		30	70	X-Stam4	N-Stam4	
		10	90	X-Stam5	N-Stam5	
		0	100	X-Stam6	N-Stam6	