Atmospheric plasma pens in polymer surface science

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Abstract

The aim of this work was preparation of uniform PS and PMMA homopolymer thin films via spin coating as well as characterization of plasma pen on the prepared samples and organic cleaned Si substrates. Modification of polymer surfaces is highly important for controlling surface properties towards the required applications such as coating. In this report some measurements aimed to verify the effect of plasma cleaning on silicon surfaces are presented. A study on contact angles for homopolymer thin films on a silicon substrate is also provided.

Contents

1. Introduction

Plasma treatment uses plasma to alter the surface of a material in order to change surface properties.

Organic surface contaminants greatly impact an object’s ability to interact with other materials.

When we plasma treat a surface, we are able to remove these contaminants. This increases the bond strength of the top layer on the object's surface. Plasma treatment generally takes about five to eight minutes. Modifications to the process can be made by introducing different gases (air, argon and helium). In this work we used two nozzles: standard nozzle and Multigas Nozzle which allow argon.

2. Experimental Methods

Plasma treatment

The plasma system used in these experiments was Plasma Wand Hand-Held Atmospheric Plasma Cleaner. Plasma treatment can achieve ultra-fine cleaning of organic contaminants from surface. The device transforms low input voltage into high electric field strengths, dissociating and ionizing the ambient process gas (typically air). The source was affixed to a stage at distances of 0.5cm, 1cm, 1.5cm from the surface of the substrate, and a scan speed of 1mm/s and 3 mm/s was used.

Materials and preparation

Polystyrene (PS) 270kD and Poly (methyl methacrylate) 250kD with thickness of 80nm was obtained via spin coating on Si substrates. In this workpure silicon was chosen as substrate. Large sheets of these silicone substrate were cut into 15 × 15 cm^2 squares and cleaned from organic contamination. Uniform thin polymer films to Si-substrate were applied by spin coating procedure using Spin Coater (SPIN coater 6-RC, SUSS Micro Tech. Lithography). Spin coating is the process of evenly coating a spinning substrate with a solution. The solution is dispensed at the center of the wafer. The thickness of film strongly depends on concentration of solution, angular speed and time of the cycle. Samples were stored in a plastic container and covered to prevent dust accumulation. At table 1 the exact parameters of sample preparation can be found.

Table1. Optimized deposition parameters
rmp is revolutions per minute, **ramp** is spinning speed, **time** is spinning duration
Concentration: PS 14 mg/1000ml in Toluene
PMMA 16 mg/1000ml in Toluene

Material	rmp	ramp	Time (s)	Approx. polymer thickness (nm)	Substrate Si
PS	4000	3	30	80±5	15×15mm2
PMMA	4000	3	30	80±5	15×15mm2

Contact angle

The OCA 35module is the base software module that enables the measurement of contact angles. Contact angles (CA) can be determined with an optical contact angle measuring and contour analysis system of the OCA series. The setup drafted in figure 1 is used to capture an image of a liquid droplet that sits on a solid (sessile drop) and to subsequently analyse it with a SCA20 software.

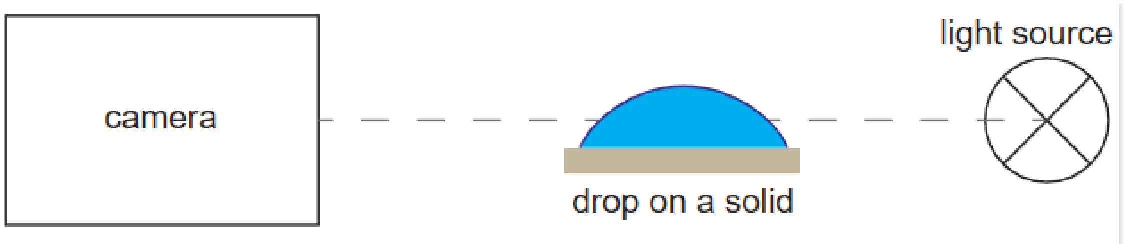

Fig1. Schematic setup for the sessile drop method

In the case of a liquid in contact with a solid and a gas the equilibrium contact angle θ_c forms at the three-phase contact line. The surface energy of the solid σ_S acts along the solid surface. The solid-liquid interfacial energy σ_{SL} acts in the opposite direction and the surface tension σ_L of the liquid acts tangential to the drop surface. The equality of vectorial forces (Fig2.) can be described by a simple scalar equation. A vector projection on the contact plane between liquid and solid yields the Young equation:

$$\sigma_L \cos \Theta_C = \sigma_S - \sigma_{SL}$$

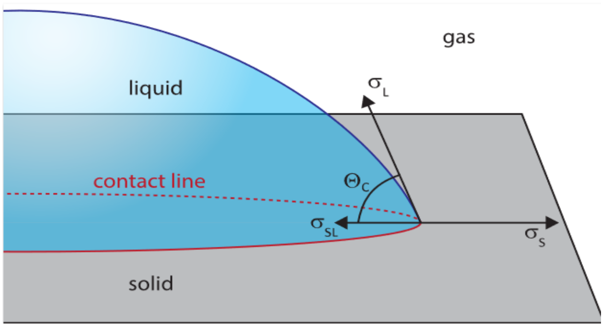

Fig2. Contact angle at a solid-liquid-gas contact line

3. Results

Temporal Evolution of CA Si organic cleaned standard Nozzle and argon nozzle

A first analysis that has been performed with CA machine is the study of the CA evolution on organic cleaned Silicon samples with two different nozzles (air, argon). Contact angles of the substrate surfaces with water droplets were measured with "DataPhysics OCA35" contact angle meter to estimate surface hydrophilicity. The effect of the atmospheric plasma exposure time on the water contact angles of PS and PMMA is shown below. The samples were treated with 1mm/s and 3mm/s of oxygen. The following equation was fitted to the contact angle data as a function of the exposure time, t, of the following form:

$$\frac{\boldsymbol{CA(t)}}{\boldsymbol{CA(t=0)}}$$

Where CA (t) is the water contact angle after plasma treatment for time *t*,
CA (0) is the silicone substrate without plasma treatment.

Table2. Parameters for the Exponential Decay Equation Corresponding to PS and PMMS
Distance between nozzle and sample 5mm

	CA(0)	CA(10s)	CA(15s)
PS	90.7	37,87	45,17
PMMA	108.6	146,2	138,63

Table3. Corresponding to PS and PMMS
Distance between nozzle and sample d=10mm

	CA(0)	CA(10s)	CA(15s)
PS	90.7	52,27	52,87
PMMA	108.6	117,97	101,63

Table4. Corresponding to PS and PMMS
Distance between nozzle and sample d=15mm

	CA(0)	CA(10s)	CA(15s)
PS	90.7	45,07	44,7
PMMA	108.6	116,4	108,7

Conclusion for tables 2, 3 and 4:
After plasma treatment the contact angle of PS was reduced to less than half. The difference between 10s and 15s of treatment should be neglected if we assume a different surface for those samples. From the three measurements, I conclude a saturation of the cleaning process between 0s and 10s. For further treatment, it will not affect the state of the sample surface.
After plasma treatment the contact angle of PMMA hasn't changes significantly. I assume no impact of plasma treatment on PMMA.
As demonstrated in the tables, the distance between sample and source doesn't have any big influence on the results

The effect of the atmospheric plasma exposure time on the water contact angles of Si substrate with different nozzle
Table 5. Corresponding to Si substrate with air and Ar nozzles
Distance between nozzle and sample d=5mm

	CA(0)	CA(10s)	CA(15s)
Si (Air)	42,06	37,57	37,5
Si (Ar)	42,06	149,2	138,7

Table6. Corresponding to Si substrate with air and Ar nozzles
Distance between nozzle and sample d=10mm

	CA(0)	CA(10s)	CA(15s)
Si (Air)	42,06	34,53	36,77
Si (Ar)	42,06	137,83	138,7

Conclusion for tables 5 and 6:
Contact angle of Si substrate after plasma treatment with standard nozzle was smaller than Si substrate without plasma treatment. But with argon nozzle it increased CA more than three times. The distance between sample and source doesn't have any important influence as in the previous results.

Roughness measurements by atomic force microscope (AFM)

Surface roughness after plasma treatment was measured on the Si substrate. The scan size by AFM can be chosen 10×10 nm. The following equation was fitted to the roughness analyses as a function of the exposure time, t, of the following form:

$$\frac{\boldsymbol{\theta_{RMS}(t)}}{\boldsymbol{\theta_{RMS}(t=0)}}$$

Where $\boldsymbol{\theta_{RMS}}$ (t) is the root means square after maximum plasma treatment, $\boldsymbol{\theta_{RMS}}$ (0) is the silicone substrate without plasma treatment.

Table 7. Corresponding to Si substrate with air and Ar nozzles
Distance between nozzle and sample d=5mm

	$\boldsymbol{\theta_{RMS}}$ (0)	$\boldsymbol{\theta_{RMS}}$ (10s)	θ_{RMS}(15s)
Si standard (air)	0,41058	0,334714	0,185629
Si etch (Ar)	0,41058	0,373359	0,401595

Table8. Corresponding to Si substrate with air and Ar nozzles
Distance between nozzle and sample d=10mm

	θ_{RMS} (0)	θ_{RMS} (10s)	θ_{RMS} (15s)
Si standard (air)	0,41058	1,81119	0,90355
Si etch (Ar)	0,41058	2,77269	2,74205

Conclusion for tables 7 and 8:
Roughness silicone substrate with distance between nozzle and sample d=5mm increased after plasma treatment with standard nozzle, but with argon nozzle hasn't changes importantly. When we change the distance roughness greatly increased in case of both nozzles. While observing two different sample distances, one can see an increase of roughness for higher distance and a decrease for lower distance. The reason for that has yet to be investigated.

Table9. Corresponding to PS and PMMS
Distance between nozzle and sample d=5mm

	θ_{RMS} (0)	θ_{RMS} (10s)	θ_{RMS} (15s)
PS	3,09115	0,787024	1,24081
PMMA	3,07267	4,5229	0,809391

Table10. Corresponding to PS and PMMS
Distance between nozzle and sample d=10mm

	θ_{RMS} (0)	θ_{RMS} (10s)	θ_{RMS} (15s)
PS	3,09115	0,575113	0,616798
PMMA	3,07267	3,80896	3.71399

Table11. Corresponding to PS and PMMS
Distance between nozzle and sample d=15mm

	θ_{RMS} (0)	**θ_{RMS}** (10s)	**θ_{RMS}** (15s)
PS	3,09115	0,502632	0,430492
PMMA	3,07267	3,10241	4,937665

Conclusion for tables 9, 10 and 11:
Roughness of PS after plasma treatment with standard nozzle was reduced three times. The difference between distance 5, 10 and 15mm of treatment should be neglected. Roughness of PMMA is increasing with plasma treatment. When we did plasma treatment with distance 5mm it's too close the sample, burning it to a smooth surface roughness changing depending on the speed velocity.

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List of parameters and samples and characterization:

Nozzle	Distance (mm)	gas	velocity /[mm/s]	sample
standard	5	air	2	Si organic
standard	5	air	3	Si organic
standard	10	air	2	Si organic
standard	10	air	3	Si organic
standard	20	air	2	Si organic
standard	20	air	3	Si organic
standard	5	air	2	PS 270kDA 80 nm
standard	5	air	3	PS 270kDA 80 nm
standard	10	air	2	PS 270kDA 80 nm
standard	10	air	3	PS 270kDA 80 nm
standard	15	air	2	PS 270kDA 80 nm
standard	15	air	3	PS 270kDA 80 nm
standard	5	air	2	PMMA 250kDA 80nm
standard	5	air	3	PMMA 250kDA 80nm
standard	10	air	2	PMMA 250kDA 80nm
standard	10	air	3	PMMA 250kDA 80nm
standard	15	air	2	PMMA 250kDA 80nm
standard	15	air	3	PMMA 250kDA 80nm
etch	5	Ar	2	Si organic
etch	5	Ar	3	Si organic
etch	10	Ar	2	Si organic
etch	10	Ar	3	Si organic
etch	15	Ar	2	Si organic
etch	15	Ar	3	Si organic