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EE412 – Final Report
Deep Trench Spray Coating

Objective

Obtain a uniform coat of photoresist at the bottom of 650µm X 350µm DRIE trenches that are approximately 350µm deep. The region of interest for lithography was the central 50 µm X 50µm region.

- Target photoresist thickness at the bottom < 3µm
- Photoresist thickness variation < 0.5µm
- Expose test patterns on spray coated wafers using ASML with the MSI patch

Final Recipe

- Resist mix : 5% SPR 220-7, 35% Ethyl lactate, 60% MEK
- Dispense rate : 9µl/s
- Pressure : 600mbar
- Passes : 12
- Chuck Temperature : 75C
- Spin speed : 30rpm. Alternated every pass
- Velocity profile : vp6 with nozzle raised 400,000 units between index 7 to 9 (see Appendix E)
- Resist thickness : 2.7µm ± 0.3µm

Introduction

A general introduction to the theory of spray coating and the tool is available in the references [1][2][3] and the SNF wiki. Deep trench spray coating and the associated deep trench exposure using ASML could open new possibilities in the fabrication of MEMS devices. The specific goal of this project was motivated out of a need to pattern the backside of a device layer in a SOI wafer without resorting to wafer bonding and layer transfer.

Substrate Preparation

Exposure testing with ASML requires that the bottom of the trenches have a mirror finish and all that trenches lie on the same plane. To achieve this, two R – prime double polished 350µm thick wafers were fusion bonded with a 0.5µm buried oxide layer using a teflon jig to align the flats. The top wafer was etched through to stop on the BOX using LTO as hard mask in sts2. The BOX was stripped in 6:1 BOE and the wafer was coated with 200nm of LPCVD silicon nitride in thermconitride. Some of the wafers were then diced into individual 8mm x 8mm dies for recipe development in the spray coater. More details on the wafer preparation procedure are given in Appendix A. Immediately before spray coating, the

substrate was cleaned in 4:1 Piranha solution at 100C for 20mins followed by HMDS vapor prime in the YES oven. All experiments were conducted within a few hour of the YES oven prime.

Recipe Parameters

All recipes used the Accumist nozzle. A summary of the range in which various parameters were varied is given below. A brief description of different parameters and their main effects on the spray coating process is given in Appendix B.

S. No.	Parameter	Range
1	Resist mixture (% by weight)	Resist (SPR 220-7) : 4.8% - 11.4% Low vapor pressure (Ethyl Lactate) : 25% - 45% High vapor pressure (Methyl Ethyl Ketone) : remaining Mixtures were allowed to stand for at least 24hrs after mixing before being used.
2	Dispense rate	3µl/s – 15µl/s
3	Nozzle pressure	300mbar - 900mbar
4	Passes	5 – 15
5	Spin speed	30rpm. Direction alternated between passes
6	Chuck temperature	75C
7	Velocity profile	Kept constant for most of the experiments. The profile used was taken from Pierre Ponce's recipe P44 and in units of stepper motor is 46, 76, 110, 154, 206, 309, 618, 309, 206, 154, 110, 76, 46 units/s. The conversion factor was calculated to be 9µm / unit. Towards the end of the project the velocity profile was adjusted to improve resist coverage and uniformity.

Table 1 : Recipe parameters

Methods

The experiments were conducted in 3 phases. For each experiment in phase I and II, a single die was taped to the edge of a carrier wafer with kapton tape. For phase III, to test different velocity profiles 3 pieces were used per experiment taped to the center, middle and edge of a wafer respectively. They were labeled as "1", "2" and "3" respectively in the experiment IDs and microscope images. After spray coating the wafer was baked at 90C for 300s.

Phase I

In the first phase, all parameters were varied over the range specified in Table 1 using a Design of Experiment (DoE) methodology. A table with all the experiments done during this phase is available in Appendix C . SEM and microscope images are available on the wiki. Resist thickness was measured from SEM images by cleaving the substrate through the trench. In this phase SEMs were obtained for all the regions marked with orange circles in Fig 1. For some experiments SEM images of the red circled regions were also obtained. However, in the interest of time this was discontinued midway through this phase.

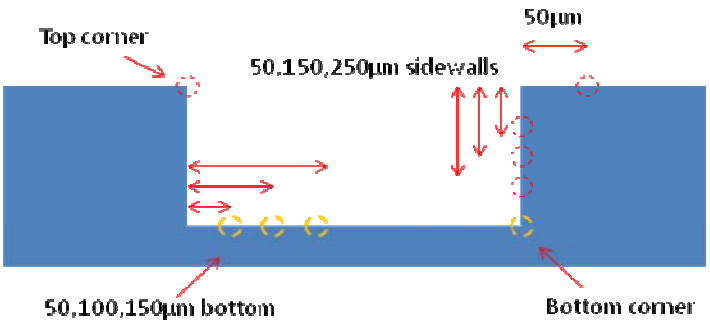

Figure 1 : SEM locations

Phase II

In the second phase, the design space was narrowed down to a smaller region based on the result from the first phase. A table with all the experiments done during this phase is available in Appendix D. The results from this and the previous phase were used to determine the best mixture for spray coating. The best film was determined by observing the optical microscope images. Films with lower roughness were considered better. For certain selected experiments the resist films were coated with 30nm of Aluminum in metallica sputter coater and imaged in the Zygo while light 3D surface profiler to measure thickness variation.

Phase III

In the third phase, the best nozzle pressure for deep trench spray coating was determined and then the velocity profile was adjusted to achieve best results in all regions of the wafer. However, while changing the velocity profile the dispense rate and passes were also adjusted to keep the amount of resist dispensed per pass approximately constant at 1ml per pass. A table with all the experiments done during this phase is available in Appendix E.

Exposure Testing

Exposure testing of spray coated resist in deep trenches required special changes to be made in ASML. ASML in normal operation can only apply focus offsets of up to 30µm. Since the trenches coated in this project were approximately 350µm, a special mode of ASML was used called the "MSI patch". In this special mode, the stepper was instructed to direct its level sensor laser to 3 predefined locations with large 10mm x 10mm trenches. Since the trenches are at the same plane as the level sensor no focus offset was applied. The pattern used for exposure were 4µm x 60µm lines spaced 12µm apart. Features were exposed with doses of 400mJ / cm^2 and 700mJ / cm^2 .Development post exposure was done manually at the Headway wet bench using MF26A developer.

Error Analysis

The major source of error was observed to be thickness measurement in SEM. At 10k magnification the error in estimating the resist to silicon and resist to air interface from the SEM image was approximately ±40nm. Since each thickness measurement consisted of two such measurements, the total error in measuring thickness was ±80nm. For a typical mean resist thickness of 1µm, the error was ±8%.

Another source of error in measuring thickness using SEM was the cleaving process. The exact location of the cleave was found to be difficult to control and as a result the mean thickness measured depended on the exact location of the cleave. This resulted in a relatively large thickness uncertainty.

Results and Discussion

Based on results from Phase I and II, the best resist mixture for deep trench spray coating was determined to be 5% SPR 220-7, 35% Ethyl Lactate and 60% Methyl Ethyl Ketone. Based on results from Phase III a nozzle pressure of 600mbar was determined to give best results. Velocity profile vp6 with the nozzle raised 400,000 units from index 7 to 9 gave the best results. However, the roughness is relatively high at the center. The velocity profile vp6 is 51, 87, 104, 140, 197, 267, 351, 1410, 351, 267, 197, 140, 104, 87, 51 units/s. For this velocity profile the best dispense rate was found to be 9µl/s. For a 12 pass recipe the film thickness was measured to be 2.7µm ± 0.3µm. The thickness variation was measured using Zygo. Microscope images for a substrate spray coated using this recipe is shown in Fig 2

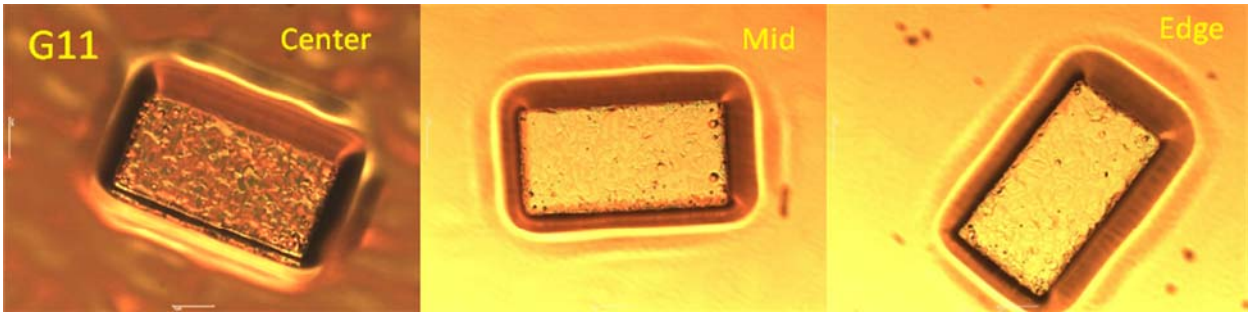

Figure 2 : Microscope images for different regions of a wafer using velocity profile vp6

It was found that slower velocity profiles resulted in a higher amount of resist sprayed per unit area per unit time. This resulted in very “wet” films which allowed the resist to flow and hence form smooth films without pinholes and voids. However, due to the higher quantity of solvent on the surface as the mixture dried, this also resulted in the film pulling back from corners and edges due to surface tension. This effect could be mitigated to some extent by lowering the dispense rate. However, EVG doesn’t recommend lowering dispense rate below 5µl/s.

It was observed that increasing the pressure keeping the velocity profile and dispense rate constant gave smoother films and prevented resist coalescing. However, too high pressure made the films rougher. The optimum pressure had to be determined experimentally for each resist mixture, velocity profile and dispense rate combination. An example of this effect for a resist mixture containing 5% resist and 25% Ethyl Lactate is shown in Fig 3.

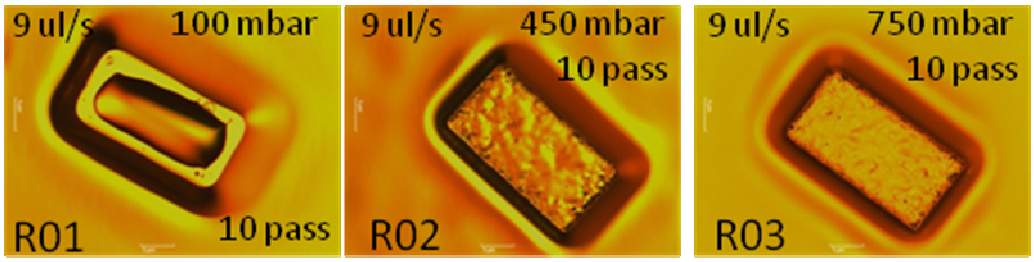

Figure 3 : Effect of increasing pressure

During exposure testing it was observed that the test images were exposed adequately in the larger 10mm x 10mm trenches with 400mJ/cm^2 of energy and 3mins of development. However, in the smaller 350µm x 650µm trenches the resist did not clear even with 700mJ/cm^2 of dosage and 5mins of development. The resist thickness at the larger trenches is close to the thickness at the top of the wafer and as a result is significantly thicker that the bottom of the smaller trenches. The spray coating process takes close to 20mins to complete during which time the wafer is placed on a heated chuck at 75C. After this the wafer is baked in a 90C hotplate for 200s. It is possible that the long spray time and the subsequent bake could have driven most of the solvent away and over – baked the resist. However, more tests will need to be conducted to confirm this hypothesis. The exposed test pattern at the bottom of 10mm x 10mm trenches is shown in fig 4

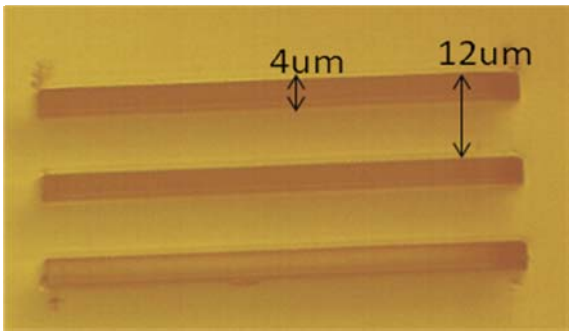

Figure 4 : Exposed test pattern at the bottom of 10mm x 1omm trenches

Conclusion

The effect of different recipe parameters was investigated on deep trench spray coating and the best set of recipe parameters was obtained by conducting numerous experiments. A resist thickness of 2.7µm ± 0.3µm was measured using SEM and Zygo for this set of recipe parameters. The film quality was qualitatively determined by observing the microscope images. Exposure testing was done with ASML stepper using the MSI patch and 4µm wide features were resolved in large 10mm x 10mm trenches. These features couldn't be resolved in the smaller 350µm x 650µm trenches even after 700mJ/cm^2 of dosage and 5mins of development.

Acknowledgements

I would like to acknowledge help and discussion with Jason Parker, Pierre Ponce, J Provine, Makoto Nakamura, Linda Ohara, Ping Ding, Vinny Pici, Mary Tang and Mahnaz Mansourpour.

References

1. Nga N Pham *et al* 2005 “Spray coating of photoresist for pattern transfer on high topography surfaces”, *J. Micromech. Microeng.* **15** pp691-97
2. Liming Yu *et al* 2006 “Spray coating of photoresist for 3D microstructure with different geometries”, *J. of Physics Conf. Series (International MEMS Conference)*,**34** pp937-942
3. Vijay Kumar Singh *et al* 2005 ”Deposition of thin and uniform photoresist on three-dimensional structures using fast flow in spray coating” *J. Micromech. Microeng.* **15** pp2339-2345

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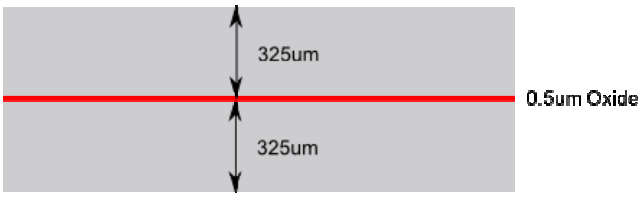
Appendix A

Substrate Preparation

Wafer Bonding

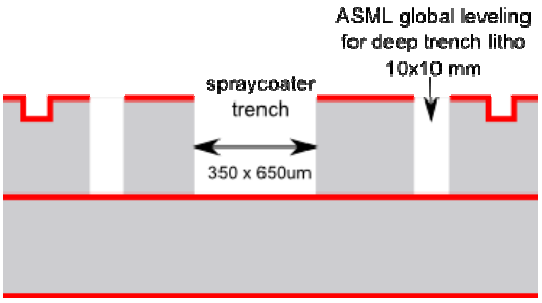


0.5um of thermal oxide was grown at 1100C on a 325µm double polished R – prime wafer. This wafer was then cleaned using the standard diffusion clean procedure for oxidation in wbdiff. After cleaning in 4:1:1 H_2O:HCl:H_2O_2 , the HCl hotpot was thoroughly rinsed and filled with 4:1:1 H_2O:NH_4OH:H_2O_2 and the wafers cleaned in it for 10mins. Care was taken to thoroughly rinse and clean during the change of chemicals since ammonium hydroxide reacts with hydrochloric acid to produce toxic chlorine gas. The treatment with ammonium hydroxide activates the surface and leaves it –OH terminated and facilitates fusion bonding. After cleaning, the wafers were dried using the SRD. The drying time was increased manually to ensure that the surfaces were free of water. Following this, the wafer flats were manually aligned using the diffusion clean teflon jig available near tylan 1-4 and a second a 325µm double polished R – prime wafer was bonded to an oxidized handle wafer. Significant manual pressure was applied to the center of the bonded wafers to ensure a good bond. The wafers were then annealed by dry oxidation at 1100C for 4 hours to complete the fusion bonding process. It is recommended to perform this procedure late at night to ensure low particle contamination in the clean room and also convenience in changing chemicals.

ASML Alignment marks

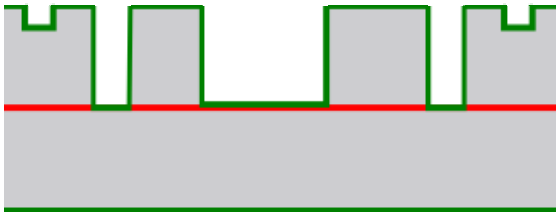
Standard ASML alignment marks were patterned on one side of the wafer.

STS2 DRIE Etching



3um LTO was deposited using tylanbpsg recipe LTO400PC. The LTO was patterned with rectangles sized 350µm x 650µm. Three larger squares sized 10mm x 10mm were also patterned. These larger squares were required for used the MSI patch in ASML for deep trench exposure. The LTO was etched in amtetcher using program #3. The resist was then stripped and the top wafer was etched through in sts2 DRIE using recipe Olav-SOI1-magnet for approximately 50mins.

Oxide Strip and Nitride Deposition



The BOX was stripped in 6:1 BOE in wbnonmetal. It was then coated with 200nm Low stress nitride in thermconitride1 using the LSN recipe for 20mins.

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Appendix B

Spray Coating Parameters

Resist Mixture

In spray coating, resist is typically mixed with a low vapor solvent (LVP) and a high vapor solvent (HVP) in varying ratios depending on the desired outcome. The solvents reduce the viscosity of the mixture allowing it to be sprayed into tiny droplets. As the droplet travels from the nozzle head to the wafer most of the HVP solvent evaporates, leaving only the LVP solvent on the wafer surface which facilitates flowing and spreading of the resist mixture.

Dispense Rate

As the nozzle passes over the substrate, the nozzle sprays resist at a constant dispense rate which can be set in the recipe. Dispense rate and velocity profile need to be taken into consideration together since together they determine the amount of resist mixture reaching the substrate. A high dispense rate combined with a slow velocity profile leads to a large quantity of resist mixture to be dispensed on the substrate. This typically leads to very smooth films. However this also leads to resist pulling back from edges and leaving them uncovered. When this happens in deep trenches, due to surface tension this can sometimes cause the resist mixture to pull back from trench edges and coalesce into droplets, leaving most of the trench exposed.

Nozzle Pressure

Nozzle pressure controls the velocity with which resist droplets are ejected from the spray coater nozzle. Higher nozzle pressure improves resist coverage in high aspect ratio trenches but also increases overall film roughness.

Number of Passes

A higher number of passes result in better coverage and lower film defects such as voids and pinholes.

Velocity Profile

The velocity profile controls the speed of the nozzle arm as it travels over a wafer. Since the center of the wafer has a lower area to be coated as compared to the edge the nozzle must spend more time at the edge and less at edge. The wafer is segmented into odd number of parts and a velocity is entered for each segment in units of the movement of the stepper motor controlling nozzle movement. The stepper motor movement was calculated to be 9 µm / unit.

Chuck Temperature

A heated chuck increases the speed with which solvents evaporates from the substrate once a resist mixture droplet falls on it. A higher chuck temperature ensures that resist doesn't get enough time to flow before most of the solvent evaporates making it highly viscous.

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Appendix C

Experiments in Phase I

Table 2 contains the paremeters, IDs of experiments and measurement results conducted during this phase. In the interest of time, only the bottom of the trenches were imaged in SEM. Microscope images were also used obtained and are available in the wiki labeled with the IDs shown below.

ID	Resist (%)	LVP (%)	Disp Rate (µl/s)	Pressure (mbar)	Pass	Bot 50 (µm)	Bot 100 (µm)	Bot 150 (µm)	Top Away 50 (µm)	Top Corner thinnest (µm)	Side 50 (µm)	Side 150 (µm)	Side 250 (µm)	Corner Bot (µm)
DE01	7.7	33.8	3	800	10	0	0	0	3.2	0.8		0	0.3	2.4
DE02	7.7	33.8	9	450	5	1.1	1.2	0.8	5.8	0.0	1.7	1.2		3.8
DE03	7.7	33.8	9	100	15	7.0	21.9	15.9	20.2	0.0	7.3	3.5	1.4	27.4
DE04	4.8	47.7	15	450	5									
DE05	4.8	47.7	3	800	10	0.5	0.5	0.4	2.1	0.0	1.3	0.4		
DE06	4.8	47.7	9	450	5	0.5	0.6	0.6	4.4	0.0	5.3	1.1	1.0	3.7
DE07	4.8	47.7	9	100	15	4.2	0.9		7.6	0.0	2.3	2.8	0.8	23.9
DE08	11.4	28.0	15	450	5	1.8	2.7	3.0	9.2	0.0	7.8	2.7	1.5	7.8
DE09	11.4	28.0	3	800	10	0.6	1.0	1.3	4.9	0.5	1.5	1.2	0.3	4.1
DE10	11.4	28.0	9	450	5	1.3	0.7	1.7	6.0	0.4	4.1	0.6	1.4	4.4
DE11	11.4	28.0	9	100	15	13.0	3.3	2.8	11.1	0.0	11.2	7.1	2.6	33.7
DE12	9.0	35.1	9	100	15	9.0	0.0	0.0	13.3	0.8	0.0	13.7	8.6	40.5
DE13	9.0	35.1	15	450	5	1.2	2.4	1.9	9.4	0.0	6.7	1.8	0.9	7.9
DE14	9.0	35.1	3	800	10	0.7	1.0	0.4	3.6	0.4	1.8	0.9	0.0	2.8
DE15	9.0	35.1	9	450	5	1.2	1.4	1.1						
DE16	9.0	35.1	15	900	5	1.0	0.5	0.7						
DE17	4.8	30.1	9	100	15	0.0	2.5							
DE18	4.8	30.1	15	450	5	1.1	1.0	1.1						
DE19	4.8	30.1	3	800	10									
DE20	4.8	30.1	9	450	5	0.8	1.1	1.0						
DE21	11.5	44.6	9	100	15									
DE22	11.5	44.6	15	450	5	1.1	0.5	0.9						
DE23	11.5	44.6	3	800	10									
DE24	11.5	44.6	9	450	5	1.3	2.3	2.1						

Table 2 : List of experiments conducted as part of Phase I

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Appendix D

Experiments in Phase II

Table 3 contains the parameters, IDs of experiments and measurement results conducted during this phase. Microscope images were used to determine the quality of the resist film.

ID	Resist (%)	LVP (%)	Disp Rate (µl/s)	Pressure (mbar)	Pass	Bot 50 (µm)	Bot 100 (µm)	Bot 150 (µm)	Corner Bot (µm)
N01	5	35	9	300	10	0.6	1.2	1.5	5.6
N02	5	35	9	450	10	1.1	1.3	1.5	6.7
N03	5	35	9	600	10	0.8	1.4	1.1	5.2
N04	5	35	12	600	10	1.3	2.6	2.9	8.4
N05	5	35	12	450	10	1.2	1.6	2.6	6.2
N06	5	35	12	300	10	0.5	1.8	3.0	9.5
N07	5	35	15	300	6				
N08	5	35	15	450	6				
N09	5	35	15	600	6				
N10	5	35	15	750	6				
N11	5	35	15	900	6				
N12	5	45	9	300	10				
N13	5	45	9	450	10				
N14	5	45	9	600	10				
N15	5	45	12	300	10				
N16	5	45	12	600	10				
N17	5	45	6	450	10				
N18	5	45	6	750	10				
N19	5	45	6	450	15				
N20	5	45	6	750	15				
N21	5	45	9	450	10				
N22	5	45	9	750	10				
N23	5	45	12	450	10				
R01	5	25	9	100	10				
R02	5	25	9	450	10				
R03	5	25	9	750	10				
R04	5	25	6	450	15				
R05	7.7	25	9	1000	10				
R06	7.7	25	12	450	10				
R07	7.7	25	9	450	10				
R08	7.7	25	9	750	10				
R09	7.7	25	12	450	7				
R10	7.7	25	12	750	7				
R11	7.7	25	9	600	10				
R12	7.7	25	9	900	10				
R13	7.7	25	9	450	10				
R14	7.7	25	9	750	10				
K01	7.7	25	9	750	10				
K02	7.7	25	12	450	10				
K03	7.7	25	9	450	10				
K04	7.7	25	12	250	10				
K05	7.7	25	12	600	10				
K06	7.7	25	15	450	6				
F01	9	30	9	450	10				
F02	9	30	9	750	10				
F03	9	30	12	450	7				
F04	9	30	12	750	7				
F05	9	30	12	1000	7				

Table 3 : List of experiments conducted as part of Phase II

Appendix E

Experiments in Phase III

Table 4 contains the parameters, IDs of experiments and measurement results conducted during this phase. Microscope images were used to determine the quality of the resist film. The different velocity profiles used are listed below. They are given in units of stepper motor movement. The conversion factor was calculated to be 9µm / unit.

- vp0 – 46,76,110,154,206,309,618,309,206,154,110,76,46 units/s
- vp1 – 106,134,254,320,440,320,254,134,106 units/s
- vp3 = vp1 x 0.5 – 53,67,127,160,220,160,127,67,53 units/s
- vp4 - 34,58,69,93,128,178,234,940,234,178,128,93,69,58,34 units/s
- vp6 = vp4 x 1.5 – 51,87,104,140,197,267,351,1410,351,267,197,140,104,87,51 units/s
- vp7 = vp6 x 2 – 102,174,208,280,384,534,702,2820,702,534,384,280,208,174,102 units/s

ID	Resist (%)	LVP (%)	Disp Rate (µl/s)	Pressure (mbar)	Pass	Velocity Profile
G01	5	35	5.5	1100	6	vp0
G02	5	35	7	450	6	vp0
G03	5	35	9	450	6	vp0
G04	5	35	9	450	10	vp0
G05/1,2,3	5	35	9	600	10	vp0
G06	5	35	9	600	8	vp0
G07/1,2,3	5	35	12	600	8	vp1
G08/1,2,3	5	35	9	600	6	vp3
G09/1,2,3	5	35	9	600	10	vp4
G10/1,2,3	5	35	9	600	10	vp6, center raised 40,000 units from index 7 to 9
G11/1,2,3	5	35	9	600	10	vp6, center raised 400,000 units from index 7 to 9
G12/1,2,3	5	35	9	1200	16	vp7, center raised 400,000 units from index 6 to 10
G13/1,2,3	5	35	16	1200	12	vp7, center raised 400,000 units from index 6 to 10
G14/1,2,3	5	35	9	600	10	vp6, center raised 400,000 units from index 7 to 9
G15/1,2,3	5	35	9	600	12	vp6, center raised 400,000 units from index 7 to 9

Table 4 : List of experiments conducted as part of Phase III