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Project acronym: SNM

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Deliverable: D5.3 ("Nanopatterning utilizing physical vapor deposited films")

Name of the coordinating person: Prof. Dr. Ivo W. Rangelow, Email: ivo.rangelow@tu-ilmenau.de

List of participants:

Participant no.	Participant organisation name	Part. short name	Activity Type	Country
1 (Co)	Technische Universität Ilmenau	**TUIL**	HER	Germany
2	EV Group E. Thallner GmbH	**EVG**	IND; End-user	Austria
3	IMEC	**IMEC**	RES	Belgium
4	Mikrosistemi Ltd	**µS**	SME; End-User	Bulgaria
5	Universität Bayreuth	**UBT**	HER	Germany
6	Technische Universiteit Delft	**TUD**	HER	Netherlands
7	Spanish National Research Council	**CSIC**	RES	Spain
8	IBM Research GmbH	**IBM**	IND; End-user	Switzerland
9	École polytechnique fédérale de Lausanne	**EPFL**	HER	Switzerland
10	SwissLitho AG	**SL**	SME; End-User	Switzerland
11	Oxford Instruments Nanotechnology Tools Ltd	**OINT**	IND; End-user	UK
12	Imperial College London	**IMPERIAL**	HER	UK
13	The Open University	**OU**	HER	UK
14	Oxford Scientific Consultants Ltd	**OSC**	SME	UK
15	VSL Dutch Metrology Institute	**VSL**	IND	Netherlands
16	University of Liverpool	**ULIV**	HER	UK

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SNM
Work Package 5
Deliverable: D5.3 ("Nanopatterning utilizing physical vapor deposited films")

Lead beneficiary number	5	**Nature**	R	**Dissemination level**	RE
Estimated Person-months	23				

Person-months by partner for the Deliverable

UBT	TUIL	IBM	OSC						
20	1.5	2	-						

Estimated Delivery Date	M38: 02/2016	**Delivery Date**	29/03/2016

Author

- Hans-Werner Schmidt and Christian Neuber

Reviewed by:

- WP5 Leader: Christian Neuber
- WPG2 Leader: Mike Cooke
- Coordinator: Ivo W. Rangelow

Criteria and Achieved Results

Criteria	**Achieved result**
Investigations on stable film formation of novel advanced molecular glass resists	Spin coated versus PVD prepared films were investigated. Spin coating works for a broad range of materials, but PVD offers distinct advantages.
Stable amorphous films and their patternability by t-SPL at IBM/SL	Stable amorphous thin films of UBT12/UBT13 or UBT8/PSS-Ph are prepared by coevaporation and show high resolution patterns.
Stable amorphous films and their patternability by FN-SPL at TUIL	Tough and robust PVD prepared film of UBT8/C_{60} mixture patterned by FN-SPL. Clear 10nm half pitch pattern are demonstrated.

Description of the Deliverable	D5.3 is focused on the investigation of solution cast and physical vapor deposited films of novel advanced molecular glass resist materials and their final application in high resolution nanopatterning. Spin coating is currently the favoured technique used for thin film preparation in lithography. It is a low cost and very fast process producing very uniform thin films. As it is widely used in industry, a lot of information on this topic exists. One main well-known advantage is that the film thickness is very easy to control and the two most crucial parameters involved, viscosity and spin-speed, are independent to each other.[1] However, spin-coating shows some limitations. A major drawback is the fact that more than 95% of the material is spin down, which is a huge economical and ecological factor. Additionally, the substrate shape is limited to small and round substrates, as large substrates cannot be spun with a sufficiently high rate and corners on rectangular substrates cause film thickness variations.[2] As the layer is formed by a spreading liquid, masks or templates cannot be used in the process, and film thickness above 200 µm are hardly realizable. Furthermore, deeply etched features cause physical obstruction preventing complete coverage or causing resist thickness variation.[3] The physical vapor deposition (PVD) process is an atomistic deposition, where the vaporized material is transported through a vacuum environment in form of atoms or molecules to the substrate. Virtually any metal or alloy as well as many organic compounds with a certain thermal stability and molecular weight can be deposited by PVD.[4] An important advantage is the possibility to measure the film thickness and the deposition rate *in situ by quartz crystal microbalances*. The typical deposition rate ranges, also depending on the material, from 1 to 10 nm/s. The film thickness can be precisely controlled from the single nanometer range to the µm range. The substrate geometry can vary from flat to complex, and by using masks intercepting the flux it is possible to produce deposition patterns on the surface. As the resulting layer is built atom-by-atom or molecule-by-molecule, any atom or molecule is deposited at the film surface and builds the current film surface until it gets covered. Because of the high kinetic energy at the surface arrival, the atom or molecule typically shows a certain mobility and has time in the order of seconds to arrange and find into a stable higher-order structure, before being covered by the following molecules. However, this vacuum deposition process can produce unusual microstructures and modifications of the material, such as amorphous films. PVD processed films also offer an excellent surface finish which can be equal to that of the underlying substrate. The absence of solvents is an ecological and economical benefit, and impurities are mostly eliminable due to a different evaporation or sublimation temperature.[5] Further advantages of PVD are the ability to create multilayer coatings simply by

sequential evaporations of different materials or material mixtures and the preparation of homogeneous material mixtures by co-evaporation of different materials.

When comparing PVD prepared films to spin-coated films, it is known that the PVD prepared films show a slightly higher density and in some cases a higher glass-transition temperature (known as ultra-stable molecular glasses).[6]

However, a drawback of the PVD process is the requirement of a fully equipped vacuum chamber and the fact that common polymeric materials cannot be processed as they decompose under these conditions.

Investigation on film forming and SPL patterning behaviour

a) Stable amorphous film forming resists

The investigation on film forming and scanning probe lithography (SPL) patterning behaviour of identified molecular glasses was an ongoing research focus since the beginning of the SNM project. As expected, some of the tailored synthesized glass forming materials showed very satisfactory film forming and long term stable amorphous films independent of utilized film preparation technique. Fig. 1 exemplarily shows the film forming of the high T_g molecular glass UBT8. Both techniques, spin coating and PVD film preparation, result in very even and stable amorphous films.

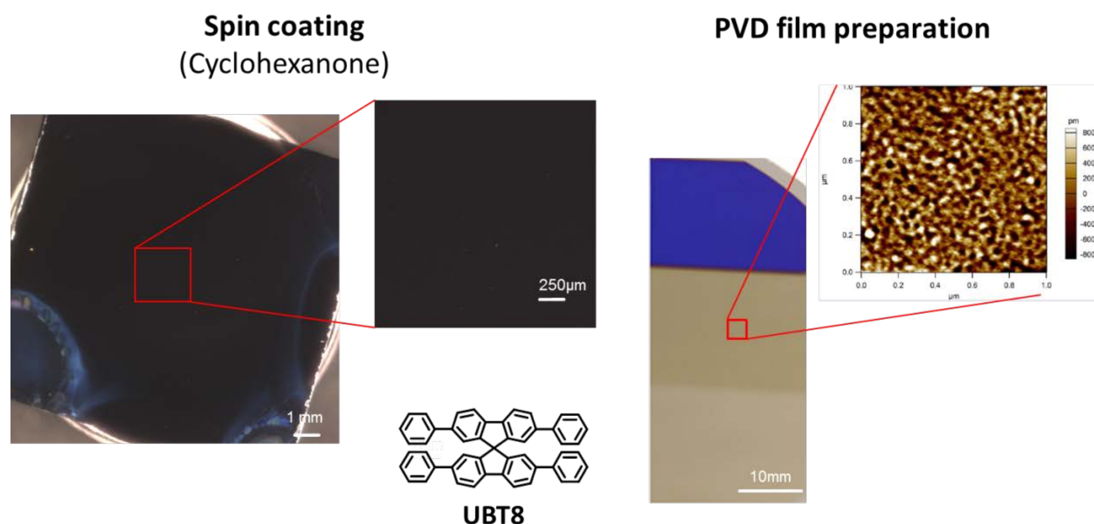


Figure 1: Spin coated and PVD prepared films of molecular glass UBT8. Both techniques result in very even and stable amorphous films.

However, high quality films did not claim high resolution SPL patterning results. Fig. 2 shows achieved features using Fowler-Nordheim SPL (FN-SPL) from TUIL (left) and using thermal SPL (tSPL) from IBM/SwissLitho (right).

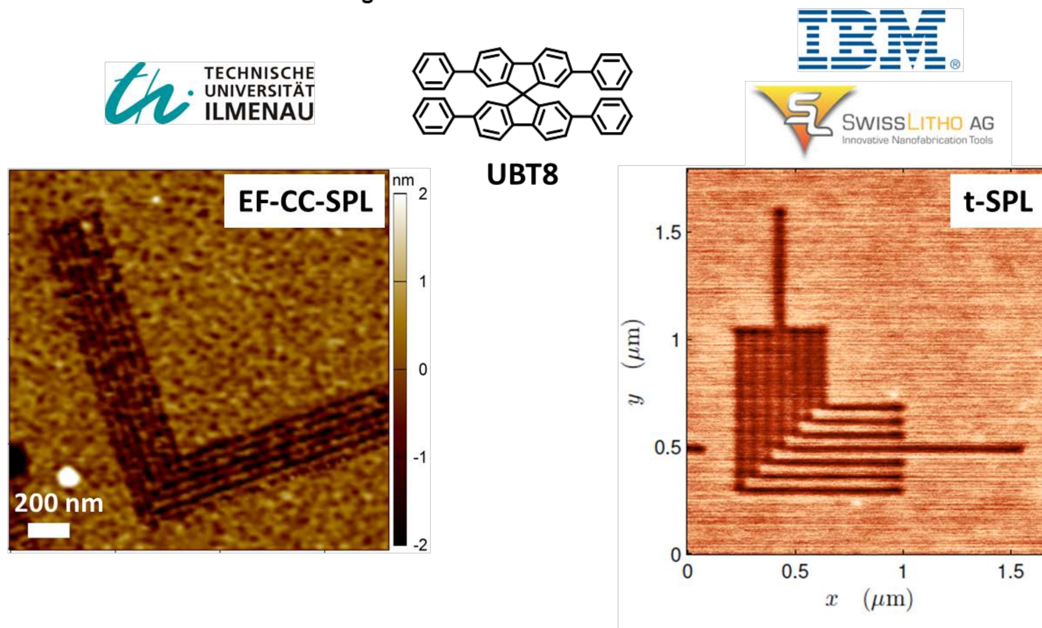


Figure 2: FN-SPL and tSPL patterned molecular glass UBT8. Films were prepared by PVD.

Neither the FN-SPL nor the tSPL technique is able to produce high resolution patterns. The FN-SPL written features show bridged and broken line features with a high line-edge roughness (LER). The tSPL written line features look blurred and high resolution patterning could not be achieved. Thus the high T_g molecular glass UBT8 with the glass temperature of 173 °C seems to be too soft under the applied writing conditions when prepared to a very thin film thickness of 10 nm or below.

A further well-known and promising molecular glass resist is the C-methylcalix[4]-resorcinarene (CMC4R). Both applied film preparation techniques shown in Fig. 3 yield thin stable amorphous film. Thus, both techniques can be used to prepare thin films of CMC4R.

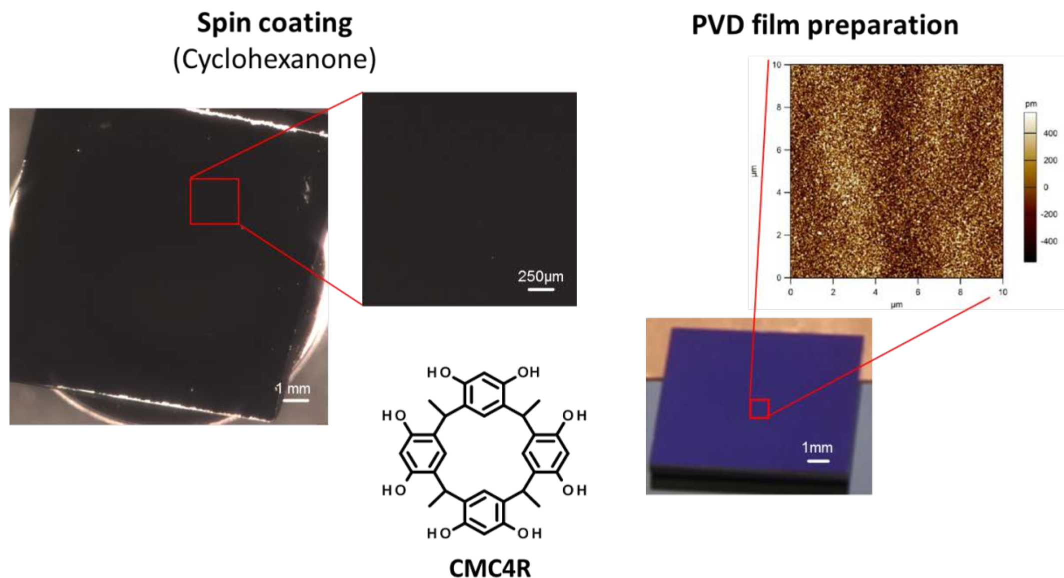
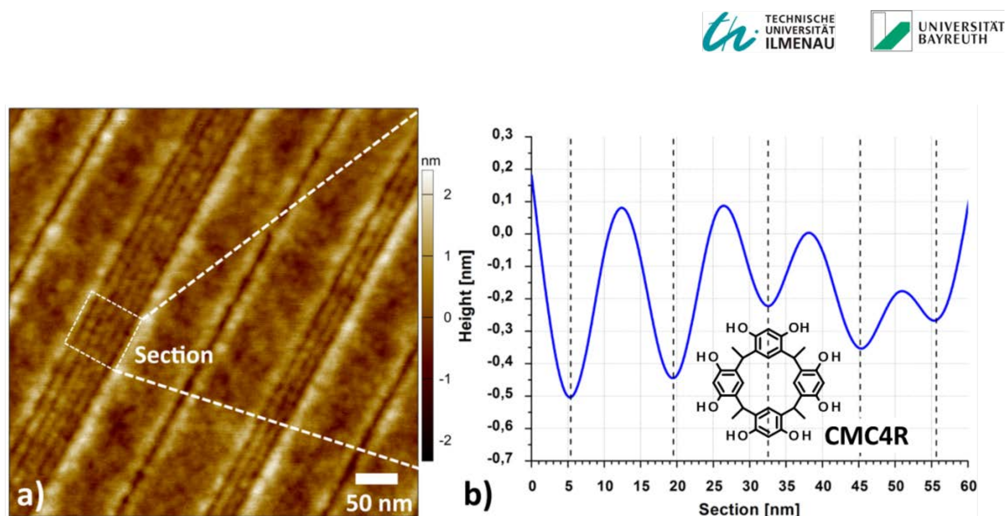


Figure 3: Spin coated and PVD prepared films of C-methylcalix[4]resorcinarene (CMC4R).

FN-SPL patterning investigations were typically done on PVD prepared thin films of CMC4R as this technique offers films without any dust particles. CMC4R works as positive as well as negative tone resist depending on the applied line dose. Fig. 4 shows high resolution line features of 7.5 nm half pitch written by the positive mode FN-SPL technique at TUIL.



High resolution patterns of 7.5 nm half pitch in CMC4R film

Figure 4: AFM topography image (2-D) with a section graph of a resolution test pattern written in 5-nm thin CMC4R film. The lines are patterned in positive-tone lithography mode (direct removal) with a pitch of about 15 nm.

b) unstable amorphous film forming resists

Beside the stable amorphous molecular glass formers there were also unstable film forming materials observed, which typically show dewetting prepared to thin films at room temperature or show such a high tendency to crystallize that only crystalline films are achieved. Fig. 5 exemplarily shows the molecular glass UBT14 with a bulk glass transition temperature at 67 °C. UBT14 shows amorphous film forming of spin coated films of a layer thickness of above 50 nm. But for thinner film thicknesses of 10 nm and below, here shown for the PVD prepared film, clearly observable dewetting at room temperature is given. In conclusion a higher T_g of above 100 °C is aimed for future investigations.

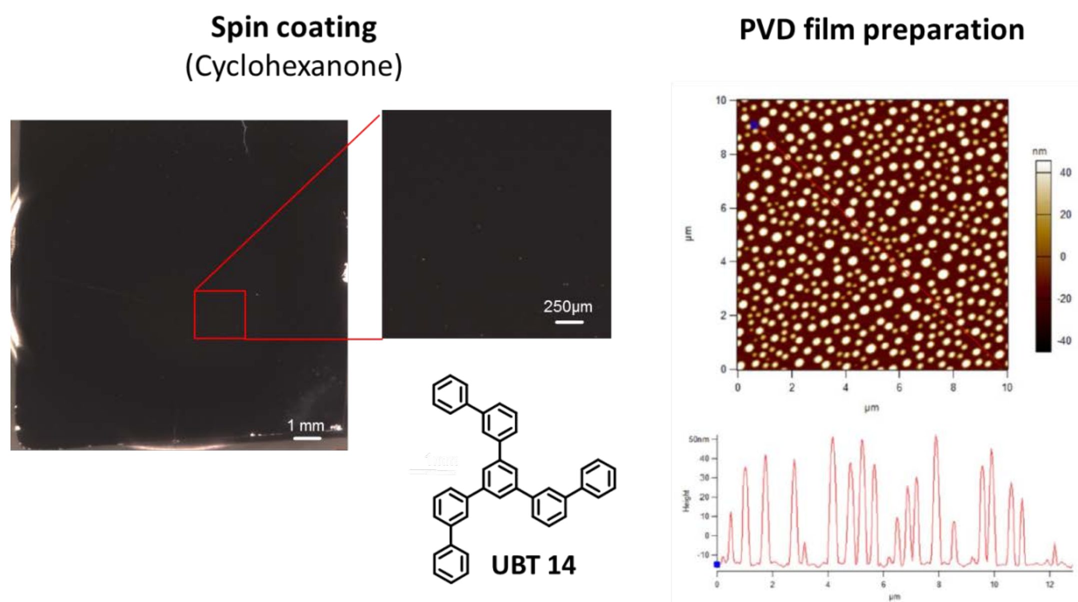


Figure 5: Spin coated and PVD prepared films of molecular glass UBT14. The thicker spin coated layer results in amorphous film formation while the very thin PVD prepared films show dewetting at room temperature.

A different film forming behaviour, well-known and expected for solution cast films, is the crystalline film formation utilizing highly symmetrical molecules. The results are exemplarily shown for the symmetrical Buckminsterfullerene C_{60} in Fig 6. The Buckminsterfullerene C_{60} shows limited dissolution behaviour in organic solvents and a very high tendency to form crystals during the solvent evaporation. Thus spin coating a C_{60} ortho-Dichlorobenzene solution results in a completely crystalline film formation. However, also a PVD prepared thin film of C_{60} shows only micro-crystals of Buckminsterfullerene molecules. The high intermolecular interaction of the very symmetrical C_{60} molecules drives them into aggregation or crystallisation.

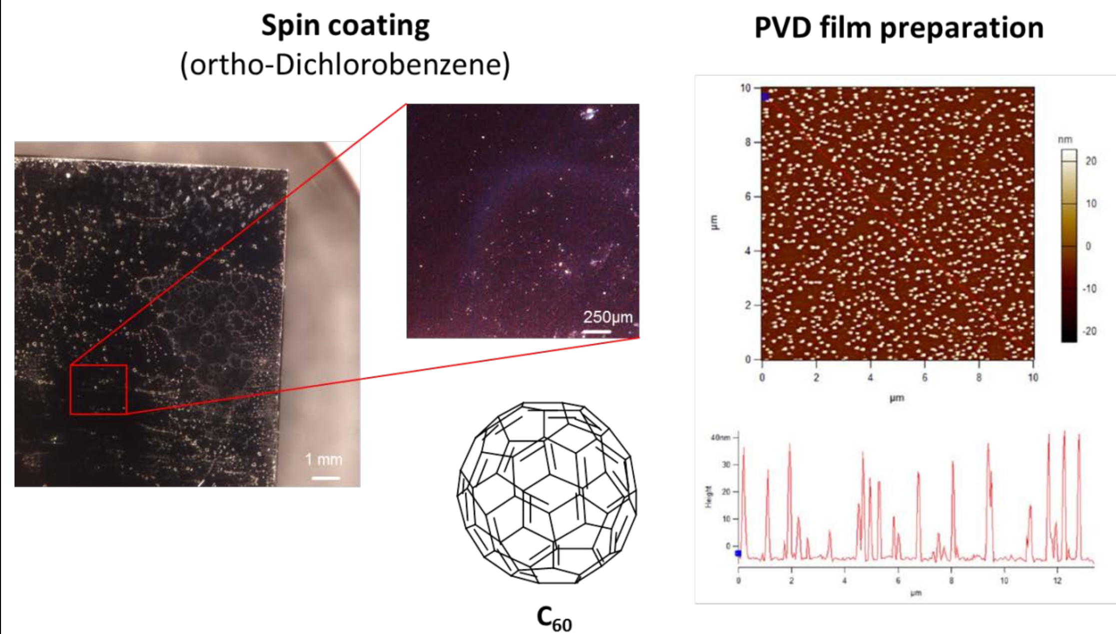


Figure 6: Spin coated and PVD prepared films of Buckminsterfullerene C_{60} .

As a consequence, the general molecular design of novel synthesized molecular glass materials was based on the very stable aromatic units which are linked by a twist, tilt, and/or rotation of other units which should reduce their tendency to crystalize. As an example the film forming properties of UBT12, shown in Fig. 7, demonstrates the still strong tendency to crystalize despite of the di-trifluoromethyl substituted outer benzene unit. Thus spin coating UBT12 results in a highly crystalline film (Fig. 7, left), while by using PVD an amorphous film can be obtained directly after the preparation. However, recrystallization occurs with time (Fig. 7, right) and limits the usability of these thin films.

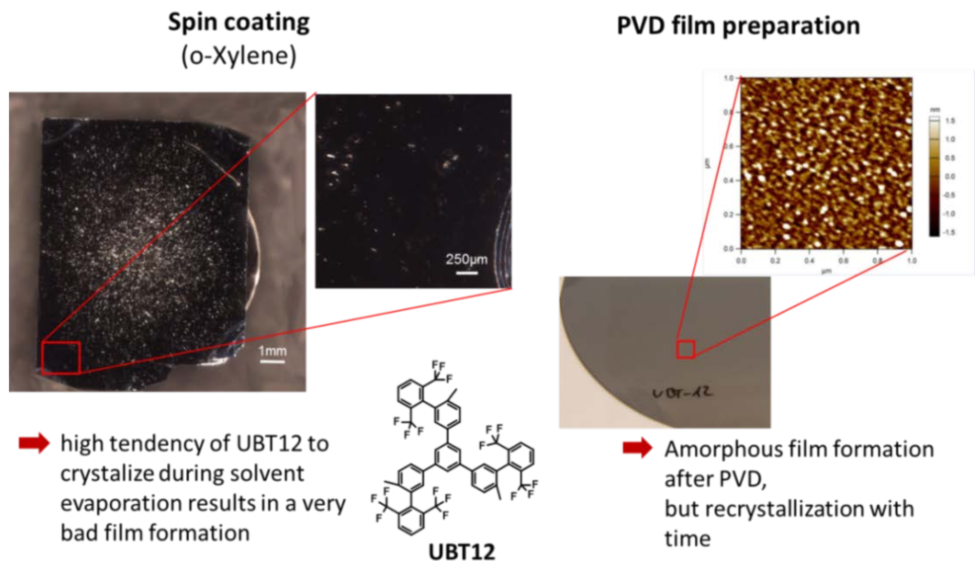


Figure 7: Film forming properties of spin coating and PVD preparation of UBT12.

c) Stable amorphous film forming resists of material mixtures

The available broad range of synthesized materials and the option of co-evaporation allowed the preparation of a stable amorphous thin film such as of a 1:1 mixture of UBT12 and UBT13. Because of the molecular similarity but distinct difference of one tri-fluoromethyl group in the outer benzene rings of both materials and the concurrent single molecule by molecule co-evaporation a stable amorphous film with similar high force sensitivity to tSPL was achieved. Fig. 8 shows high resolution patterns of a PVD prepared thin film of the 1:1 mixture of UBT12/UBT13.

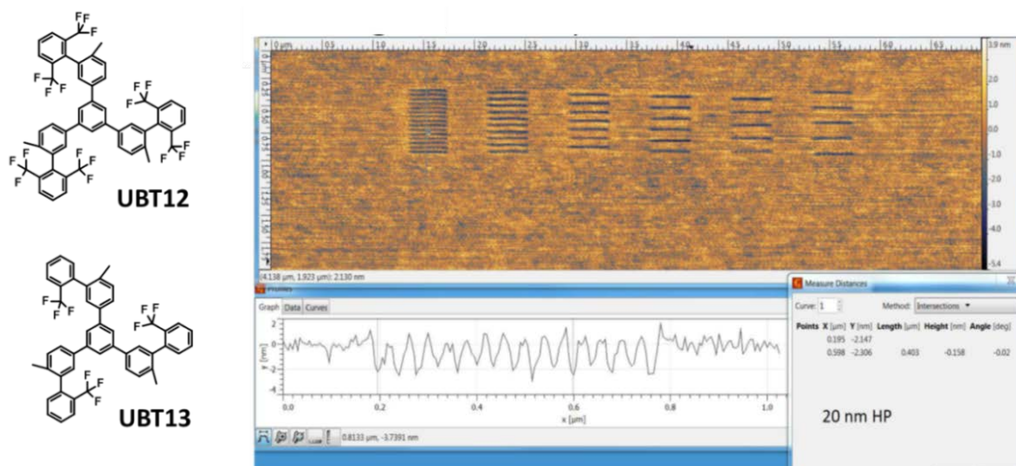


Figure 8: High resolution tSPL line features of 20nm half pitch and larger utilizing a PVD prepared thin film of 1:1 mixture of UBT12 and UBT13. This mixture showed a stable amorphous film formation and high force sensitivity in the tSPL process.

Beside these molecular glass resists silicon rich molecular glass systems were investigated as this material class can be directly used as a hard mask for the pattern transfer. However, film forming investigations showed a completely crystalline film forming behaviour of selected Si rich materials PSS-Me, PSS-iPr, and PSS-Ph. Fig. 9 shows the film forming property investigations on spin coating and PVD preparation of PSS-iPr.

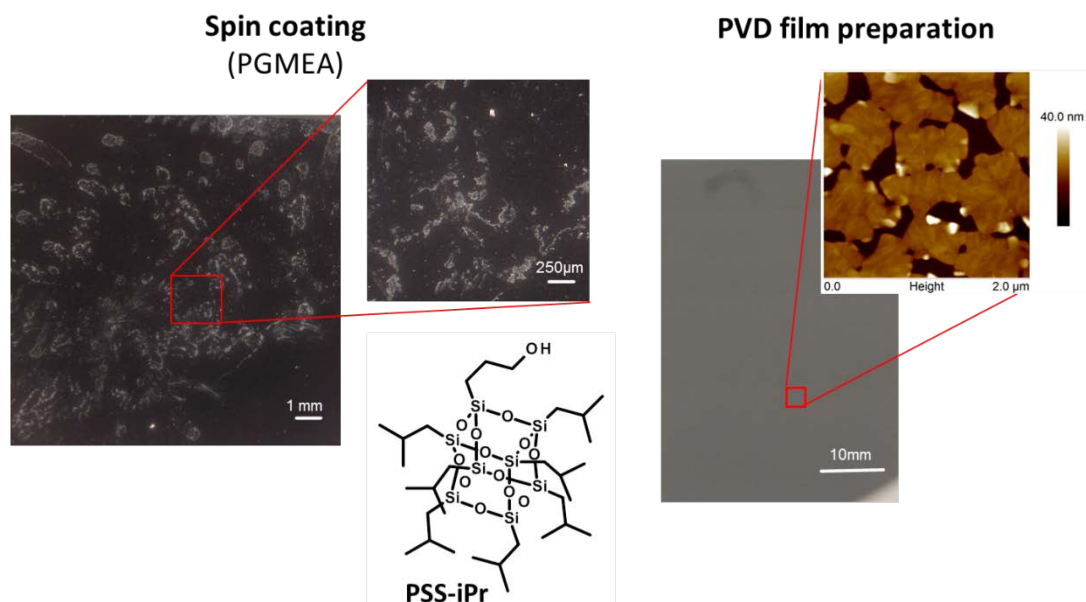


Figure 9: Film forming property investigations on spin coating and PVD preparation of Si rich material PSS-iPr. Independent of applied film preparation technique crystalline films were achieved.

Nor spin coating neither PVD film preparation showed amorphous films. The high symmetry of the silsesquioxane core results in the observed high tendency to form crystalline films. Similar film forming properties were observed for PSS-Me and PSS-Ph.

Based on the finding that co-evaporation of two compatible materials could form a stable amorphous film, a 1:1 mixture of PSS-Ph and UBT8 was coevaporated at different layer thicknesses (see Fig. 10).

PVD film preparation of silicon rich molecular glass resist

Wafer: Si + HM (8006, 50nm)

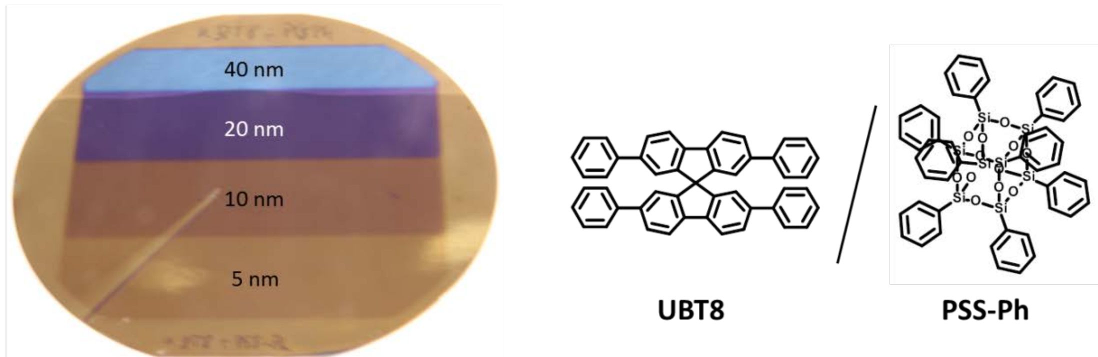
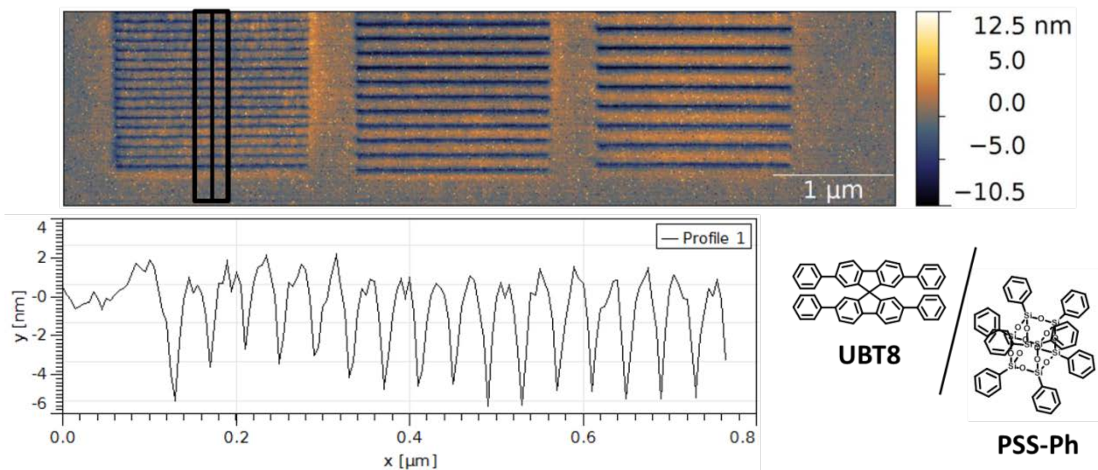


Figure 10: Image of 4 inch wafer with a step layer thickness gradient of a 1:1 mixture of UBT8 and PSS-Ph.

The tSPL patterning potential of this high etch resistant Si rich molecular glass has been demonstrated by IBM/SwissLitho. 20 nm half pitch line features were written into a 5 nm thick layer of a mixture of Si rich molecules PSS-Ph and UBT8 (see Fig. 11).

t-SPL of UBT8/PSS-Ph resist



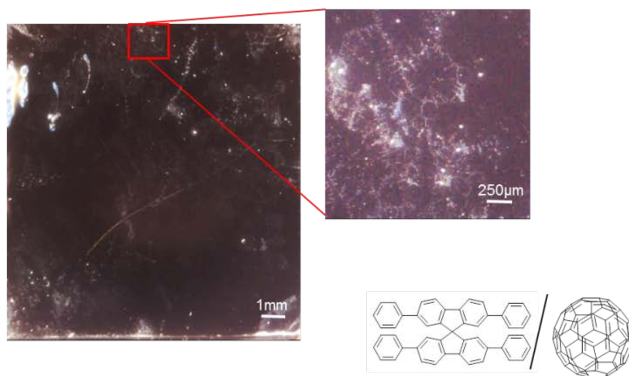
20 nm half pitch lines in 5 nm PSS-Ph/UBT8 film

Figure 11: Thermal-SPL patterning at IBM/SwissLitho utilizing a PVD prepared 5 nm thick film of a 1:1 mixture of UBT8 and PSS-Ph. 20 nm half pitch line features are demonstrated.

The potential of this high etch resistance of Si rich molecular glass has been demonstrated by transferring by oxygen reactive ion etching (RIE) 60 nm half pitch lines, patterned into a 5 nm thick layer of a mixture of Si rich molecules PSS-Ph and UBT8 spiro resist material, into the underling 50 nm thick HM8006 resist layer. During the etch transfer the in-situ generated SiO_2 hard mask and in addition 10 nm of the underling HM8006 resist layer are removed. Thus, the resulting HM8006 transfer layer was 40 nm thick.

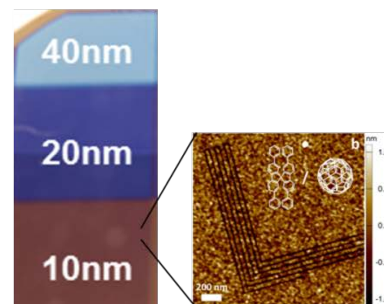
Because of the very promising etch performance of the polymeric fullerene containing resists from OSC we developed a fullerene containing molecular glass resist. But again the high tendency of the Buckminsterfullerene C_{60} to form aggregates or crystals was a challenge to prepare stable amorphous films. Here the strategy was to mix the very crystalline and the not easily dissoluble C_{60} with an amorphous co-resist. Because of the fully aromatic character of the C_{60} fullerene the fully aromatic resists UBT8 and UBT14 – UBT17 offered promising miscibility. Due to the high T_g of 173°C UBT8 was favored. Fig. 12 shows the thin film formation investigations of a 1:1 mixture of UBT8 and C_{60}. The high tendency of C_{60} to crystalize during solvent evaporation results in a very bad film formation during spin-coating, while by co-evaporation of UBT8 and C_{60} uniform and very even thin films of different layer thicknesses and with a surface area roughness of 0.260 nm are prepared (Fig. 12).

Film preparation via spin-coating
(dichlorobenzene solution)



➡ high tendency of C_{60} to crystalize during solvent evaporation results in a very bad film formation

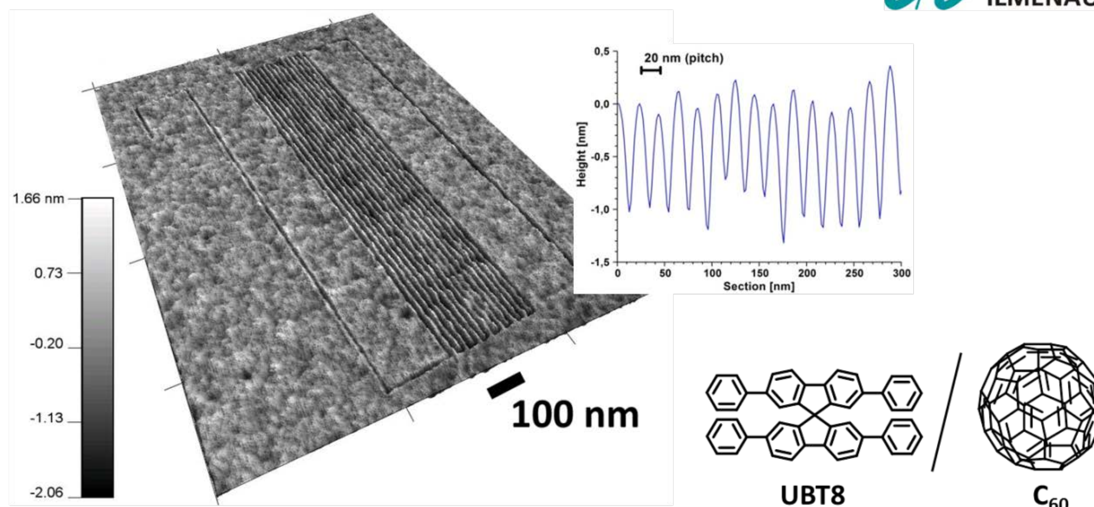
Film preparation via PVD



➡ uniform and very even thin films of different layer thickness

Figure 12: Thin film formation investigations of 1:1 mixture of UBT8 and C_{60}. The high tendency of C_{60} to crystalize during solvent evaporation results in a very bad film formation while by co-evaporation uniform and very even thin films of different layer thickness can be prepared.

First preliminary FN-SPL pattern shows absolutely clear corner features with a half pitch of 25 nm and a very clear imaged film surface. Thus high resolution patterns of dense line features of 10 nm half pitch utilizing the co-evaporated 1:1 mixture of UBT8 and C_{60} were realized (Fig. 13). The clear 10 nm half pitch lines demonstrate the high potential of this straight forward development and successful improvement of resist materials for FN-SPL.



High resolution patterns of dense 10 nm half pitch in UBT8/C_{60} film

Figure 13: AFM-AC-mode topography image of closed loop positive tone patterned corner features with half pitch 25 nm of PVD prepared pure UBT8 (a) and co-evaporated UBT8/C60 (b) using the SPL-tool.

Conclusion

It is demonstrated that a stable amorphous film formation is always an issue for novel developed or synthesized resist materials and has to be optimized or tailored with respect to the thin film thickness of 10 nm and below. Spin coating is a well-known and established film preparation techniques and works for a broad range of materials, but PVD is an alternative technique for a high-quality thin film preparation and opens the possibility to fabricate novel resists systems by solvent-free co-evaporation. An impressive demonstration is given by the mixture of UBT8 and C_{60} which could only be prepared in a stable amorphous phase by co-evaporation and allows high resolution FN-SPL patterning combined with a high etch resistance.

Explanation of Differences between Estimation and Realisation	IBM and SL will focus their pattern activities on their well-known and optimized PPA [poly(phthalaldehyde)] resist for the reproducible preparation of high resolution devices. Beside the UBT8/C_{60} mixture TUIL will mainly focus their pattern activities on their well-known and high-resolution CMC4R (C-Methylcalix[4]-resorcinarene) resist for the reproducible preparation of high resolution devices.
Metrology comments	Layer thickness measurements were realized by a mechanical profilometer and the values are given are a average out of at least three individual measurements at different positions.

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