Funded by
the European Union

Collaborative project

Project acronym: SNM

Project full title: "**Single Nanometer Manufacturing for beyond CMOS devices**"

Grant agreement no: 318804

Deliverable: D5.4 ("Evaluation report about tailored molecular glass resists")

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

<table>
<tr><td colspan="7">SNM
Work Package 5
Deliverable: D5.4 (“Evaluation report about tailored molecular glass resists”)</td></tr>
<tr><td>Lead beneficiary number</td><td>5</td><td>Nature</td><td>R</td><td>Dissemination level</td><td colspan="2">PU</td></tr>
<tr><td>Estimated Person-months</td><td colspan="6">20</td></tr>
<tr><td>Person-months by partner for the Deliverable</td><td colspan="6">
<table>
<tr><td>UBT</td><td>TUIL</td><td>IBM</td><td>OSC</td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>10</td><td>0,85</td><td>2,7</td><td>-</td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
</table>
</td></tr>
<tr><td>Estimated Delivery Date</td><td colspan="2">M48: 12/2016</td><td colspan="2">Delivery Date</td><td colspan="2">23/12/2016</td></tr>
<tr><td>Author</td><td colspan="6">• Hans-Werner Schmidt and Christian Neuber</td></tr>
<tr><td>Reviewed by:</td><td colspan="6">• WP5 Leader: Christian Neuber
• WPG2 Leader: Mike Cooke
• Coordinator: Ivo W. Rangelow</td></tr>
<tr><td rowspan="3">Criteria and Achieved Results</td><td colspan="3">Criteria</td><td colspan="3">Achieved result</td></tr>
<tr><td colspan="3">Synthesis of tailored molecular glass resists</td><td colspan="3">A huge series of different molecular glasses tailored for the requirements of certain patterning techniques were synthesized and provided to the partners.</td></tr>
<tr><td colspan="3">Stable amorphous film preparation</td><td colspan="3">Spin coated versus PVD prepared films were investigated. Spin coating works for a broad range of materials, but PVD offers distinct advantages. A crucial advantageous is the coevaporation of two immiscible materials.</td></tr>
</table>

	Patternability by t-SPL at IBM/SL, FN-SPL at TUIL, and LAO at CSIC	Systematically planned patterning investigations allowed the identification of distinct requirements of resist materials.
	Etch investigations at OINT, IMEC, and TUIL	Etch behavior screening of a broad range of molecular glass resists together with commercial available polymeric standard resists allows the identification of highly promising etch resistant resists. The developed UBT8/C_{60} resist shows qualities of a promising patternable hard mask, applicable for cryogenic plasma etching. Here, ultra-thin (≤10nm) resist layers of UBT8/C60 are capable to transfer features with selectivities of more than 8:1 into the underlying Si, combined with an anisotropic etching profile.

Description of the Deliverable

D5.4 summarizes synthesis, characterization, and evaluation of tailored molecular glass resist materials over the full project period.

Synthesis, characterization and film forming behavior of novel molecular glass resists

At the project start it was known that C-methylcalix[4]resorcinarene (CMC4R) is patternable with promising results by the Fowler-Nordheim scanning probe lithography (FN-SPL) at TUIL, and IBM had patterned only a small amount of non-optimized molecular glass resists by t-SPL (thermal scanning probe lithography). In addition, molecular glass materials out of the stock of UBT were identified and used for a first material screening. These twisted, fully aromatic compounds (UBT1-UBT5, see Table 1) showed high chemical and thermal stability, featured high glass transition temperatures T_g, and formed amorphous thin films.

Parallel to the first material screening novel molecular glass materials were tailored synthesized based on the propeller shaped spiro core. This architecture shows a low tendency of crystallisation and typically a high glass transition temperature because of the rigidity of this core unit. The spiro core was directly substituted with perfluorinated benzenes or benzene units giving materials with stable amorphous film formation properties, very high glass transition temperatures at different levels of intermolecular interactions (materials UBT7 and UBT8, Table 1). Additionally, materials with added amide linkages between the spiro core and the benzene substituents were synthesized, which are able to form hydrogen bridges and thus have very strong intermolecular interactions (UBT9 and UBT10, Table 1).

However, even for materials with a high T_g such as UBT5 and UBT7, it was observed that 10 nm thick films exhibit dewetting on the silylated wafer surface. In consequence, the film

forming and the toughness of the required thin films have to be improved further for SPL patterning. Together with IBM a novel molecular glass class was discussed based on 1,3,5-tris-substituted benzene core. The tailored synthesized resist materials UBT11 – UBT21 are shown in Table 1. Unfortunately, a lot of these resists show completely crystalline thermal behavior with high melting points or in the case of amorphous phase behavior a low T_g, which was characterized by differential scanning calorimetry. Thus, at a first sight they seemed to be useless for investigation as thermal patternable resist material. But after film preparation by PVD amorphous or semi-crystalline films were achieved, which were provided to IBM. However, due to strong tendency to crystallize these films showed a recrystallization with time.

A new strategy to suppress the crystallization was realized by preparing a resist of mixed molecular glasses produced by coevaporation of two related but distinct different tris-substituted twisted materials (more details on thin film preparation by PVD see D5.3). Indeed, preparing a material mixture of UBT12 and UBT13 was a straightforward optimization to obtain stable amorphous films while the pure materials showed crystalline film forming behavior. As a consequence, the next generation of molecular glass materials was based on material combinations or mixtures to form stable amorphous films with higher toughness and increased performance. In this context the fully aromatic propeller shaped spiro UBT8 with a very high glass transition of 173 °C was selected as amorphous compound and coevaporated together with the rigid Buckminsterfullerene C_{60}. As a highlight the prepared mixture out of highly crystalline C_{60} molecules formed an amorphous thin film of high toughness in combination with UBT8.

Based on the finding that low T_g molecular glasses show surface mobility in thin films or have not the right toughness for repeated reading runs by t-SPL, the idea evolved to develop crosslinked molecular glass resists. Here, the crosslinking was realized on the one hand by covalent bindings, given by a thermally reversible Diels-Alder cyclisation between the molecular glass resist molecules and on the other hand by strong intermolecular interactions, meaning strong dipole-dipole interaction of cyano-groups. The investigated dienophile component for the Diels-Alder reaction was based on a maleimide derivative and analogous substituted as the diene component (table 1, Diels-Alder resist). Investigations of the Diels-Alder reaction by Fourier transform infrared spectroscopy (FTIR) measurements showed that the Diels-Alder reaction takes place already at room temperature. But the reaction conversion is very small and it can be increased by increasing the temperature. As a consequence, a detailed investigation on the annealing conditions for the Diels-Alder reaction was realized. The optimized conditions were observed at 1h@70°C, 3h@80°C. Using these annealing conditions the reaction rate is as high as possible and the equilibrium of the Diels-Alder reaction is driven to the product side. At higher temperatures the retro Diels-Alder reaction is more favored, and the evaporation of unreacted or regressed monomers was observed. However, the typically obtained conversion was at 65% and thus only small oligomers are present instead of high molecular weight polymer or crosslinked resist material. The second investigation was conducted on molecular glass resists with

strong intermolecular interactions. Here, the molecular glasses UBT26, UBT33, and UBT34 were synthesized and characterized. UBT26 is highly symmetric and thus a crystalline material. However, UBT33 and UBT34 form stable amorphous thin films. The highest glass transition temperature at 210°C is observed for the 1:1 mixture of UBT26 and UBT34. This ultra-high T_g makes the mixture very promising for t-SPL patterning investigations.

In a further approach Si rich molecular glass systems were investigated and directly used as a patternable hard mask. As Si rich materials commercially available silsequioxane derivatives were selected and investigated (see table 1). The high symmetric molecular architecture of silsequioxanes allowed only the formation of crystalline films independent of the utilized film preparation method. Thus again, coevaporation of two molecular compounds offered the preparation of stable amorphous thin films. The potential of high etch resistance of Si rich molecular glasses has been demonstrated by transferring a patterned film of a mixture of Si rich molecules PSS-Ph and UBT8 spiro resist material (see table 1) into the underling HM8006 layer by oxygen reactive ion etching (RIE). The resulting HM8006 transfer layer can be used for a dry etch transfer into Si (for more details see WP5 third technical report).

In further investigations novel synthesized molecular glasses (UBT22-UBT25 and UBT27-UBT32) for tip-based interactions using local anionic oxidation (LAO) were developed. Here, the synthetic strategy was to develop simple oxidizable resists which undergo an oxidative coupling during LAO. The first generation of molecular glasses UBT22-UBT25 and UBT27-UBT29 were based on the ortho-substituted biphenyl core, while the second generation uses the efficient oxidizable ortho-substituted binaphthyl unit (UBT30-UBT32). The film formation using these resist materials is possible either by spin coating or physical vapor deposition. Current investigations demonstrate that the novel molecular glass resist UBT30 can be oxidatively coupled and thus polymerized or crosslinked by LAO and offers a first negative type resist for this patterning technique. The patterns can be developed by standard organic developers and the Si substrate lying underneath was insignificantly oxidized during the LAO, meaning the resist film acts as protecting layer for the Si surface.

In summary, several generations of different molecular glasses tailored for the requirements of certain patterning techniques and a dry etch process available in the SNM project were synthesized, characterized and straight forward optimized in a feedback loop using the obtained results of the patterning and etching partners.

Funded by
the European Union

Table1. Snap shot of current molecular glass resists database summarizing investigated resist materials of the SNM project.

Name	chemical structure	comment	Tg [°C] (glass transistion temperature)	Trec [°C] (recrystallisation temperature)	Tm [°C] (melting point)	T-5wt% (mass loss of 5wt% at thermogravimetric analysis)	PVD (vapor depositable)	film formation	additional Informations
CBP (4,4'-Bis-(carbazol-9-yl)biphenyl)		matrix material for OLEDs	62 Advanced Materials 2007, V19(6), P862-866				yes		
UBT1			106	174	234		yes		
UBT2			107				yes		
UBT3			102		233		yes		
UBT4			120	201	276 (first and second heating/ no cr at cooling)		yes		
UBT5			120		233 (first heating)		yes	stable amporphous film forming	
UBT6 (PHOST)		Reference material: Mn = 25.000 g/mol					no		
UBT7			100	135	249	≥ 290	yes		
UBT8			173		267	432	yes		
UBT9							no		
UBT10							no		
CMC4R (C-methylcalix[4]-resorcinarene)		Aldrich	84 Chem.Mater, (2008) 20, p. 7292				yes		spin-coating solvent: methyl isobutyl ketone
4M1AC6 4-Methyl-1-acetoxycalix[6]arene		Aldrich							spin-coating works
Calix[4]arene					335 Thermochimica Acta, 426 (2005) 33–38 314 (TGA AT)	≥ 240	165°C		
4-tert. Butyl-calix[4]arene					335 Thermochimica Acta, 426 (2005) 33–38 346 (TGA AT)	≥140	185°C		

Funded by
the European Union

Name	chemical structure	comment	Tg [°C] (glass transition temperature)	Trec [°C] (recrystallisation temperature)	Tm [°C] (melting point)	T-5wt% (mass loss of 5wt% at thermogravimetric analysis)	PVD (vapor depositable)	film formation	additional Informations
4-tert. Butylthia-calix[4]arene					320-322 J. Molecular Structure, 655 (2003) 435-441 **357 (TGA AT)**	**≥ 330**	215°C		
TNB (1,3-bis(1-naphthyl)-5-(2-naphthyl)benzene)			72 S.F. Swallen et al. Science, 315 (2007) 353	-	-	-	yes		
TCB 1,3,5-Tris(N-carbazolyl)benzen		[148044-07-9] Aldrich: 1 g: 102 €	122	**140-247**	325-330 (Aldrich)		n.a.		
TCTA 4,4',4''-Tri-9-carbazolyltriphenylamin		[139092-78-7] TCI Europe: 1 g: 49,75 €	152 (J. Mater. Chem., 2010, 20, 8126)	237 (J. Mater. Chem., 2010, 20, 8126)	179-183 (Aldrich) 298-301 (Sensient) 266 (J. Mater. Chem., 2010, 20, 8126)	**≥ 440**	n.a.		DSC
Spirobischromane (6,6',7,7'-Tetrahydroxy-4,4,4',4'-tetramethyl-2,2'-spirobichroman)		oxidation sensitive			270 (decomposition) Journal of Chemical Society (1939) p. 195-199		yes		
Spirobisindane (5,5',6,6'-Tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-spirobisindane)					315 (decomposition) Journal of Chemical Society (1934) p. 1678-1681		yes		
Trisphenol (α,α,α'-Tris(4-hydroxyphenyl)-1-ethyl-4-isopropyl-benzene)			94 Chem. Mater. 20 (2008) p. 1606				yes (slightly decomposition)		
4,4'-(1-α-Methyl-benzylidene)-bisphenol			58 Chem. Mater. 20 (2008) p. 1606				n.a.		
UBT11			-	291	357		yes		
UBT12				281	316		yes		
UBT13			-	316	364		yes		
UBT14			67		140		yes	melts only at first heating	
UBT15			101	169	273		yes		

Funded by
the European Union

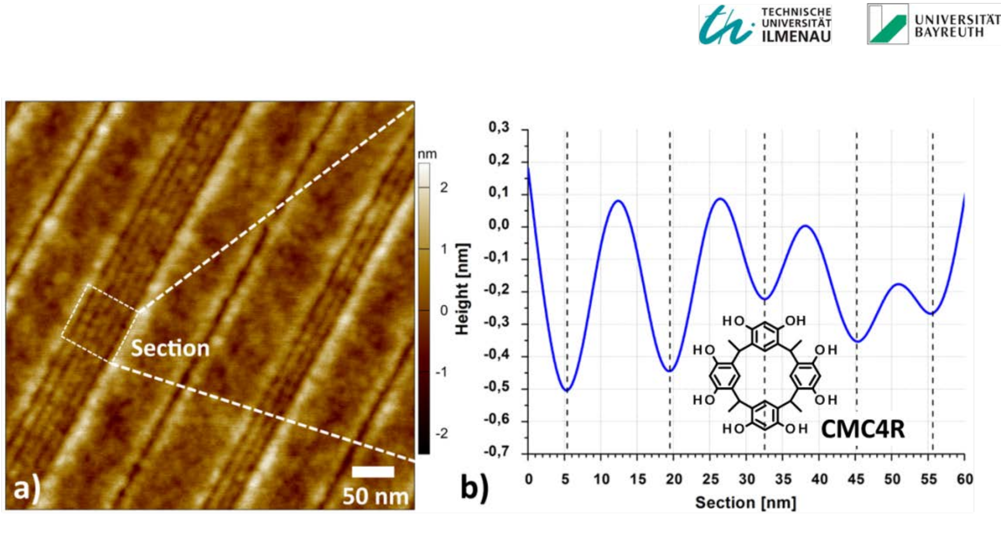
Name	chemical structure	comment	Tg [°C] (glass transition temperature)	Trec [°C] (recrystallisation temperature)	Tm [°C] (melting point)	T-5wt% (mass loss of 5wt% at thermogravimetric analysis)	PVD (vapor depositable)	film formation	additional Informations
UBT16			84	_	_		yes		
UBT17				274	290		yes		
UBT18				281	320 and 326		yes		
UBT19			10		159		yes		
UBT20				241	264, 282		yes		
UBT21			78	105	230		yes		
UBT22			1		112				
UBT23				197	237		yes	high surface roughnes (Rq = 0.62nm) of PVD prepared film	
UBT24			71	-	-		yes	low surface roughnes (Rq = 0.21nm) of PVD prepared film	
UBT25			84	136, 219	250		yes		
UBT26					400°C unter Zers.		yes	complete crystalline films	
UBT27			94	_	-	≥ 300	yes		
UBT28			86	_	203	≥ 400	yes		
UBT29			95	_	197	≥ 350	yes		
UBT30			_	_	_	≥ 350	yes		

Name	chemical structure	comment	Tg [°C] (glass transition temperature)	Trec [°C] (recrystallisation temperature)	Tm [°C] (melting point)	T-5wt% (mass loss of 5wt% at thermogravimetric analysis)	PVD (vapor depositable)	film formation	additional Informations
UBT31			89	–	–	≥ 400	yes		
UBT32			112	–	236	≥ 400	yes		
UBT33	Molecular Mass = 492.526 u		165	–	320	420	yes		
UBT34	Molecular Mass = 568.621 u		198	–	340	450	yes		
Diels-Alder resist			–	–	–	–			
C60		TCI					yes	strong aggregation, highly cristalline film on native Si-wafer	
PSS-Ph		Aldrich					290°C	PVD prepared films looks amorphous, but shows micro-crystallinity	
PSS-Me		Aldrich					130°C	Substrate has to be cooled to -10°C during PVD. PVD prepared films show micro-crystallinity.	
PSS-isobutyl		Aldrich					160°C	amorphous film formation, but dewetting and recrystallisation	
PSS-octavinyl		Aldrich						no film formation on the substrat at RT of substrate	

Investigation on SPL patterning behavior

a) FN-SPL patterning investigations at TUIL

At the starting of the SNM project it was well-known that FN-SPL patterning works well with calixarene derivatives such as CMC4R. CMC4R behaves as a positive as well as a negative tone resist depending on the applied line dose. Thus, one of the first investigations was focused on the thin film preparation by PVD utilizing CMC4R. Figure 1 shows high resolution line features of 7.5 nm half pitch written by the positive mode FN-SPL technique at TUIL into PVD-prepared CMC4R films



➡ High resolution patterns of 7.5 nm half pitch in CMC4R film

Figure 1: AFM topography image (2-D) with a section graph of a resolution test pattern written in 5 nm thin CMC4R film prepared by PVD. The lines are patterned in positive-tone lithography mode (direct removal) with a pitch of about 15 nm.

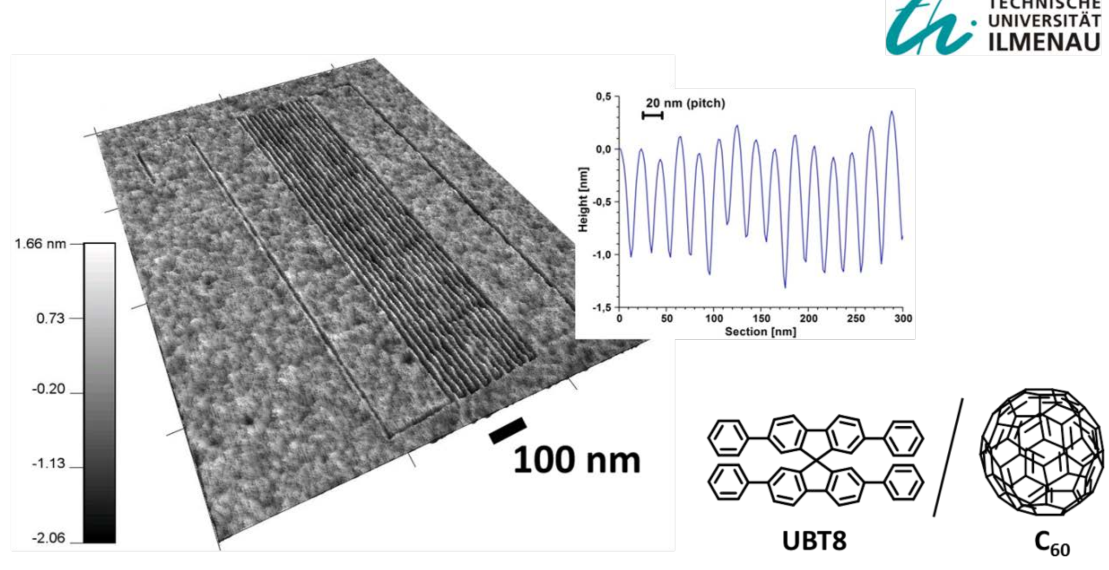
During the SNM project period a lot of patterning investigations on the fully aromatic resists developed and synthesized at UBT were performed. Based on these investigations first interesting trends with respect to material requirements for FN-SPL at TUIL were identified. In this context, the investigation on the spiro based molecular glasses UBT8 and UBT 9 with the latter containing additionally four amide linkages showed similar positive tone corner features for both materials patterned at very similar line doses. The introduction of strong dipole moments by the amide groups shows no influence on the FN-SPL patterning performance. The required line doses were slightly higher for both UBT8 and UBT9 as compared to the TUIL standard resist CMC4R. In contrast to CMC4R the molecular glasses UBT8 and UBT9 cannot be successfully patterned in a negative tone manner, whereby the fluorine containing molecular glass resist UBT7 shows promising negative tone patternability. Here, the fluorine content seems to play a very important role for negative tone patterning using FN-SPL. This finding is supported by the observation that UBT12 with its high fluorine content also behaves only as negative tone resist. In conclusion, the new investigated molecular glass resists, unlike the calixarene based MG resists, cannot be used for both positive and negative patterning, but the selected resist materials show promising distinct patterning capabilities: positive or negative tone depending on the functionalization of the molecules.

Because of the very promising etch performance of the polymeric fullerene containing resists from OSC (for more details see D 5.2) UBT developed a novel fullerene-containing molecular glass resist. Due to the high tendency of the Buckminsterfullerene C_{60} to form aggregates or crystals, it was a challenge to prepare stable amorphous thin films. Here, the

strategy to mix the very crystalline and not easily dissoluble C_{60} with the amorphous co-resist UBT8 was successful. UBT8 was selected since the fully aromatic character allows a close molecular relation to C_{60} fullerene and UBT8 offers a high T_g of 173°C. The coevaporation of a 1:1 mixture of UBT8 and C_{60} offered uniform and very thin films of different layer thicknesses with a surface area roughness (RMS) of 0.260 nm.

FN-SPL pattern investigations show absolutely clear corner features with a half pitch of 10 nm and a very clear imaged film surface. Thus, high resolution patterns of dense line features of 10 nm half pitch utilizing the coevaporated 1:1 mixture of UBT8 and C_{60} were realized (Figure 2). The absolutely stable clear 10 nm half pitch lines demonstrate the high potential of this straight forward development and successful improvement of resist materials for FN-SPL within the SNM project.

As the available AFM imaging did not allow the mapping of feature depths (see Figure 2), TUIL tried hard to observe such high resolution features by a SEM cross section. However, even with numerous attempts on lines written as long as possible, no cross sections of fractured line features were obtained. (Sections after cryogenic plasma etching of larger features were successful, see Figure 8).



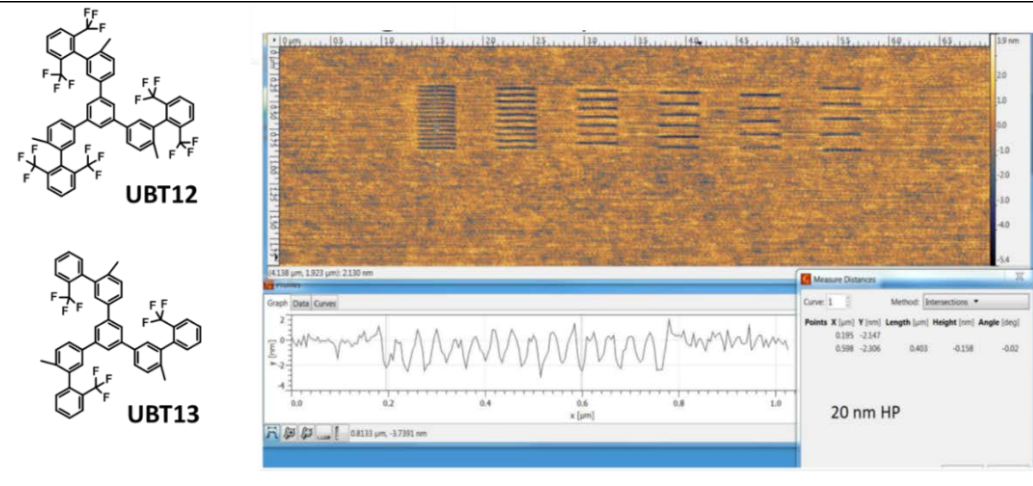
➡ High resolution patterns of dense 10 nm half pitch in UBT8/C_{60} film

Figure 2: AFM-AC-mode topography image of closed loop positive tone patterned corner features with half pitch 10 nm of PVD prepared UBT8/C_{60} thin film.

b) t-SPL patterning investigations at IBM and SL

The available broad range of newly developed and synthesized molecular glass resists and the option of coevaporation offered a detailed investigation on the requirements of resists usable in t-SPL.

The first generation of molecular glass resists (UBT1–UBT5) showed t-SPL patternability, but the prepared thin films with layer thicknesses of 10 nm and below showed a certain softening or surface mobility of these resists. This observation can be explained by the utilized very low film thicknesses, where the bulk properties strongly decline due to the domination of interface effects. Thus the strategy was followed by the tailored synthesis of higher T_g propeller shaped spiro based materials. Nevertheless, even these synthesized resists show softening during the thermal writing process, despite the increased intermolecular interactions by fluorination or the high bulk glass transition temperature of up to 173 °C. Thus, the investigated amorphous films of UBT7 and UBT8 did not allow very high resolution capability. As a consequence, to prevent softening the toughness of the required thin films has to be improved for thermal patterning. Unfortunately, investigations on the UBT8/C_{60} mixture did not show promising results for t-SPL as the fullerene molecules could not be removed and were deposited in immediate vicinity to the line features. Together with colleagues at IBM a novel molecular glass class was discussed based on 1,3,5-tris-substituted benzene core. The newly developed and tailored synthesized resist materials are summarized in table 1, UBT11-UBT21. Unfortunately, most of them show completely crystalline thermal behaviour with high melting points and amorphous film formation was not expected. But after film preparation by PVD amorphous or semi-crystalline films were achieved, which were provided to IBM. The first patterning investigations utilizing UBT12 offered high force sensitivity and line features of 11 nm half pitch. However, with time recrystallization of PVD prepared thin films of UBT12 were observed. Here the broad range of synthesized materials of UBT11–UBT21 and the option of coevaporation allowed the preparation of a stable amorphous thin film of a 1:1 mixture of UBT12 and UBT13. Because of the molecular relation, but distinct difference of one tri-fluoromethyl group in the outer benzene rings of both materials and the concurrent single molecule by molecule coevaporation, a stable amorphous film with similar high force sensitivity to t-SPL, as observed for UBT12, was achieved. Fig. 3 shows high resolution patterns of a PVD prepared thin film of the 1:1 mixture of UBT12 and UBT13.



Stable film formation of the PVD prepared 1:1 mixture

Figure 3: High resolution t-SPL line features of 20 nm 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 t-SPL process.

Besides these molecular glass resists novel silicon rich molecular glass systems were developed and investigated. This material class can be directly used as a hard mask in a subsequent pattern transfer. A stable amorphous film was only achieved by coevaporation of two compatible materials, the 1:1 mixture of PSS-Ph and UBT8, and offered 20 nm half pitch line features written into a 5 nm thick layer. The potential of this high etch resistance of Si rich molecular glass has been demonstrated by transferring 60 nm half pitch lines by oxygen reactive ion etching (RIE), patterned into a 5 nm thick layer of a mixture of Si rich molecules PSS-Ph and UBT8 spiro resist material, into the underlying 50 nm thick HM8006 resist layer.

The large number of investigations on the molecular glass resists clearly demonstrates that this class of material is influenced by the thermal process during t-SPL and the non-functionalized resists show softening independent of the achieved high T_g of 173 °C for UBT8. As a consequence, the IBM standard polymeric PPA resist shows distinct advantages as compared to molecular glass resists and is still used by IBM and SwissLitho. This conclusion creates the idea to develop a resist system which is enforced either by supramolecular chemistry or by covalent bonds. The concept of supramolecular chemistry was realized by the introduction of strong dipol-dipol interactions of cyano groups (see table 1, UBT26, UBT33, and UBT34). The synthesized UBT33 and UBT34 show a very high T_g of 165°C and 198°C, respectively. However, the coevaporated stable amorphous 1:1 mixture of UBT26 and UBT34 features a T_g of 210°C. The first t-SPL patterning tests are under investigation and should show a better patternability, if the supramolecular chemistry is an alternative way to increase the pattern performance of t-SPL.

The strategy to use covalent bonds between molecular glasses in t-SPL resist was pursued by developing a new evaporable Diels-Alder resist (see table 1). Here, the molecular glass film

was prepared by PVD and the resist was linked covalently by a thermal annealing step at lower temperatures. The thermo-reversible covalent Diels-Alder linking could be opened again at higher temperatures as available by t-SPL. Unfortunately, the maximal conversion achieved at low temperature annealing was 65% and thus only small molecule combinations are yielded. However, an annealed film of the Diels-Alder resist was sent to IBM/SL and they carried out first patterning. The results show the patternability of this film, but also residues are observed around the patterned area. Because of the mentioned very low molecular weight of the molecule combinations, similar to the investigated molecular glass resists, softening of the film could be an explanation (for more details see WP5 fourth technical report).

In summary the investigations demonstrate that the molecular glass resists are alternative candidates for t-SPL featuring high resolution patterning, but the highly optimized polymeric PPA resist from SwissLitho and IBM still offers an enhanced patterning performance.

c) LAO patterning investigations at CSIC

The third patterning technique, for which molecular glass resists were developed and synthesized, is called LAO (Local Anodic Oxidation). For these investigations the series of UBT22-UBT25 and UBT27-UBT32 were tailored and synthesized (see table 1). Standard non-coated silicon AFM probes have been used (TESPA R3, Bruker). The humidity control system works by introducing dry or wet nitrogen air into the AFM chamber to set it in the range of 20% - 60% relative humidity (RH). The sequence for writing a pattern was as follow:
(1) The AFM is operated in soft tapping mode, with an oscillation amplitude of around 15 nm.
(2) The AFM tip is moved to the position in order to start the patterning of a line.
(3) The feedback-loop is disconnected, and a positive bias voltage is applied to the sample through the AFM chuck.
(4) The tip is moved along the line at the selected speed.
(5) When the tip reaches the end of the line, the bias voltage is switched to zero, and the feedback loop is connected.
(6) The tip is moved to the new position to create the next line.

In order to hold tip−surface separation constant, the lines are fabricated following the direction where the lateral movement of the tip is parallel to the surface.

First investigations demonstrated that the synthesized molecular glass resists could be oxidative coupled and thus molecular changed by LAO. Unfortunately, some thin film showed dewetting and some stripping at the wet development step. However, UBT30 with its promising binaphthyl core shows a clear and efficient patternability and development in THF/cyclohexane mixture (see Figure 4).

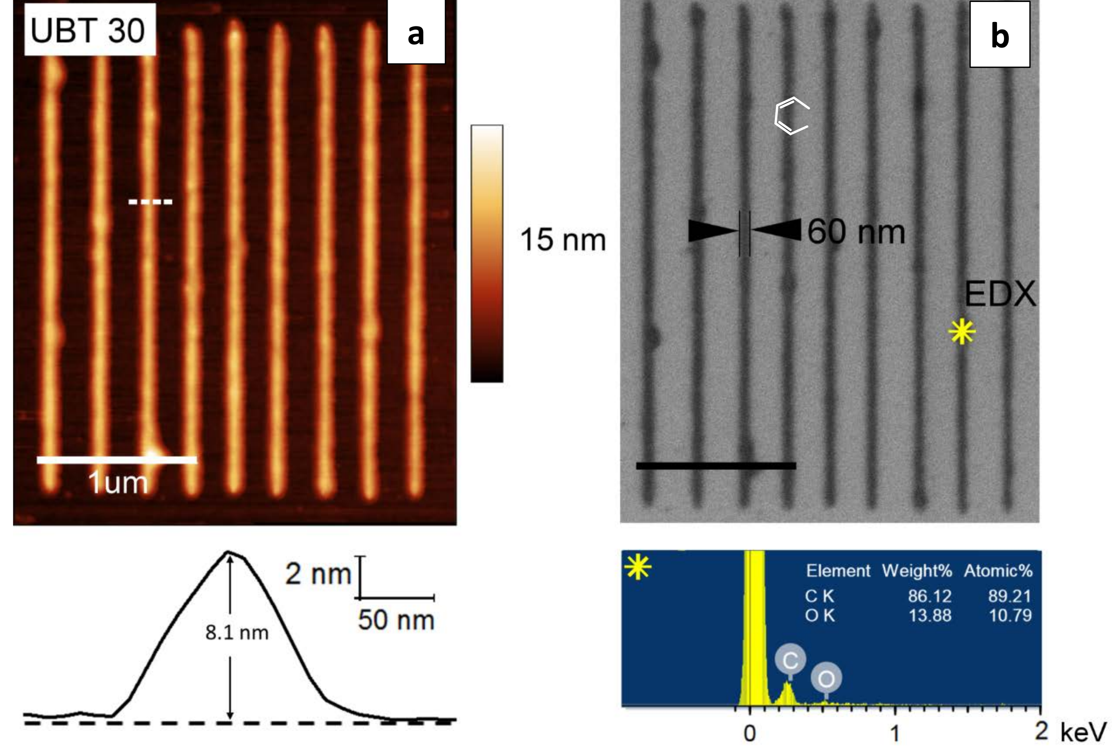


Figure 4: a) *Local anionic oxidation nanolithography using a 7nm thick film of UBT30. UBT30 allows an efficient coupling by LAO patterning and b) wet development in a 1:3 THF/cyclohexane mixture. The EDX analysis demonstrates that the underneath Si substrate is protected by the molecular glass resist and non-oxidized by the LAO process.*

EDX analysis of LAO patterned area (Figure 4) shows the native character of the Si-layer underneath. Thus no detectable or only less oxidation of the Si substrate underneath is generated by the LAO process while the molecular glass resist is patterned in a negative manner.

In conclusion a novel negative type molecular glass resist was developed for LAO. The patternability and development behavior was investigated and optimized. The molecular glass resist protects the Si surface to oxidation during the LAO process and thus allows the patterning of resist surfaces without oxidation of the Si surface.

Investigation on dry etch behavior of molecular glass resists

Alongside with patterning the dry etch resistance of molecular glass resists in comparison to standard reference resist systems was investigated. Here, the first focus was on the identification of the basic etching behavior and the structure material etching behavior relationships with respect to their thermal behavior and molecular architecture. Figure 5

summarizes the first identified fully aromatic molecular glass resist materials, which were investigated together with Polyhydroxystyrene (PHOST) and commercially available ArF and KrF photoresists as reference polymeric resist material. All materials were systematically screened for their etch behavior in typical Si etch (ICP discharges HBr, O_2, Cl_2, and SF_6), as well as to typical dielectric etch (CCP discharge, CF_4-based).

This first screening demonstrated a clearly improved etch resistance of molecular glass films compared to the Polyhydroxystyrene (PHOST), as well as to ArF and KrF reference photoresists. In addition, first investigations concerning “cryogenic etching” were also promising as no signs of resist cracking were observed even at cooling to -120°C.

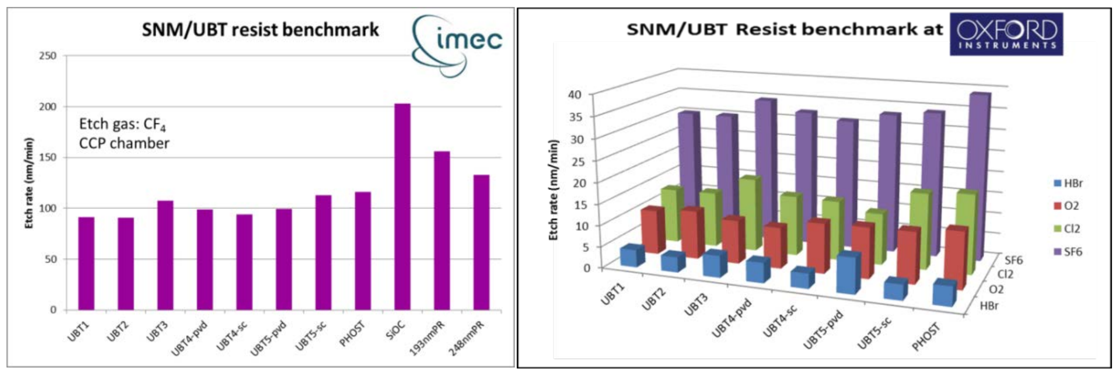


Figure 5: Etching behavior investigation on molecular glass resist by OINT and IMEC. Molecular glass resist materials are promising candidates for pattern transfer as etch selectivity is significantly improved compared to reference polymeric resists.

In further etching investigations more and more molecular glass resists were investigated and distinct material trends were worked out (see Figure 6). The UBT5, UBT7, and UBT10 with high fluorine contents feature higher etch rates as compared to their molecular related resists, when etched in fluorine rich etch gas. UBT11 – UBT13 exhibit a higher etch resistance under the noticed etch conditions due to their strong tendency towards crystallization. In addition, investigations dealt with the film preparation techniques and the post apply bake. Here, physical vapour deposited and solution cast resists were compared with each other and different post apply bake temperatures were applied to PVD prepared films. No clear influences in dependence of the film preparation technique or the applied post apply temperatures were identified. As a consequence, annealing of PVD prepared molecular glass resist films is not giving a influence on their etch performance and thus also to the overall film properties. However, an outstanding etch resistance of the fullerene containing polymer resist MFHM1 was observed. Surprisingly, the molecular glass mixtures of UBT8 and UBT14 also shows a promising high etch resistance. While the pure molecular glasses UBT8 and UBT14 show etch rates of 89 nm/min and 104 nm/min, respectively, the 1:3 ratio of UBT8:UBT14 features an etch rate of 46 nm/min.

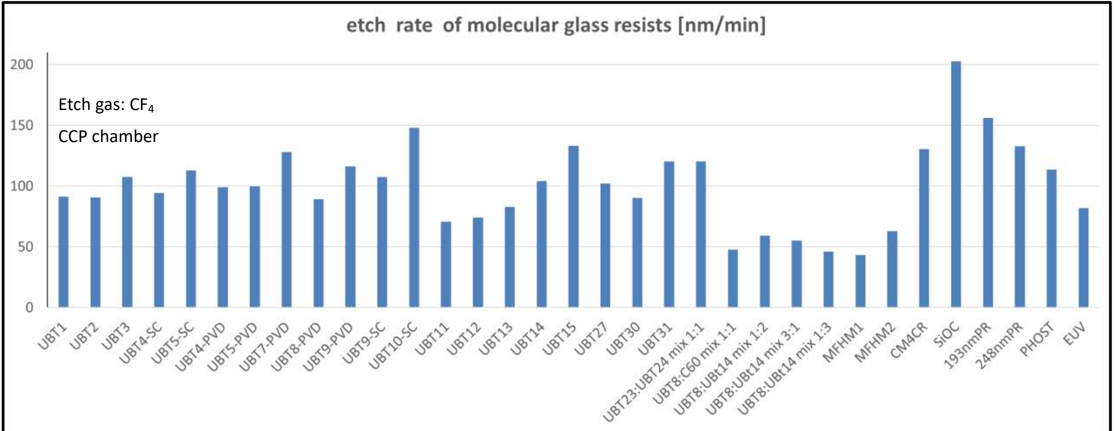


Figure 6: Overview of etch investigations on reference resist materials and molecular glass resists.

In addition, IMEC and UBT conducted a more detailed investigation on the film properties of etched resist layers. Therefore, films of UBT8 and the reference PHOST were prepared at UBT and etched off to about half of the initial layer thickness at IMEC. The idea was to investigate Gel Permeations Chromatography (GPC) and High Pressure Liquid Chromatography (HPLC) to identify higher molecular weight materials originating from the crosslinking during the plasma treatment. However, we observed only a highly crosslinked insoluble skin on top of the etched off layer and native resist material below. We were able to transfer flakes of the crosslinked skin to substrates and to measure their thickness and surface area roughness (for more details see WP5-second technical report).

Based on the outstanding etch resistance of the fullerene containing resist MFHM1 the idea to mix the high T_g molecular glass UBT8 with the Buckminsterfulleren C_{60} was born. The limited solubility of C_{60} and the strong tendency to crystallize required the coevaporation of both materials. The FN-SPL patternability is reported above and the currently done etch investigations demonstrate the excellent resist performance of the UBT8/C_{60} mixture. Using CF_4 as etch gas a very low etch rate of 48 nm/min was measured at IMEC. When using an etching gas mixture of N_2/H_2, which is preferentially used to etch the amorphous carbon hard mask layer APF, nearly nothing of the UBT8/C_{60} resist film thickness disappears, while the CMC4R was removed by the etch rate of 120 nm/min (see Figure 7).

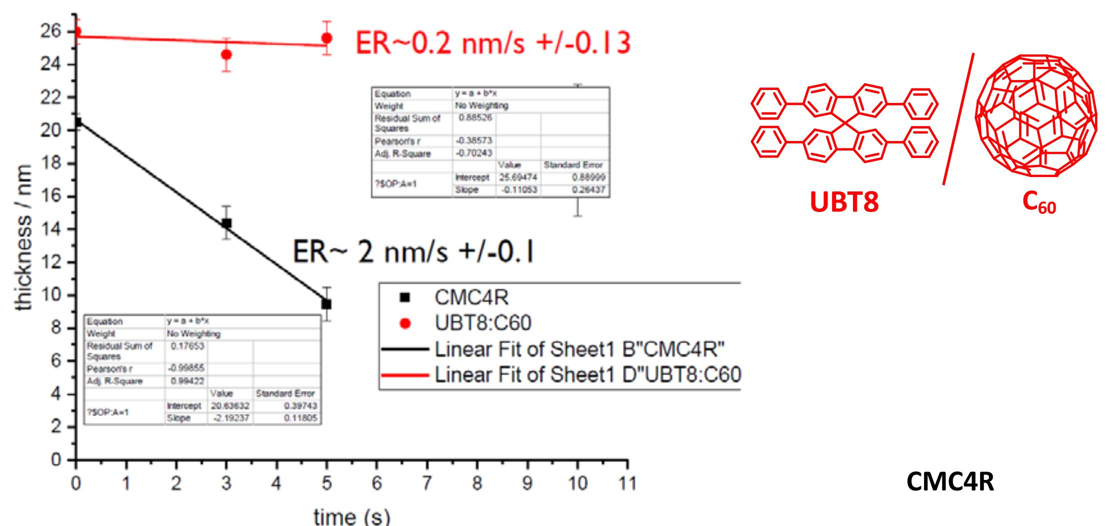


Figure 7: Etch investigations on the molecular glass resist mixture UBT8/C_{60} and CMC4R. Both resists demonstrate high resolution patternability in E-field SPL. The PVD prepared films were used without any additional thermal treatment.

Motivated by these findings TUIL conducted cryogenic plasma etching using SF6 / O2 chemistry at -120°C (Tool: Oxford Instruments Cobra Tool) on FE-SPL patterned pillars (see Figure 8). The investigations demonstrate that by applying only 10 nm thick UBT8/C60 resist layers (without a hardmask stack) etching depths of more the 100 nm for large area patterns are reachable. In case of patterning sizes below 100 nm an etching depth of 85 nm was achieved. Selectivities between 8:1 – 15:1 (Si:Resist) were obtained. In addition, the side-view SEM image (Figure 8-a) demonstrates an anisotropic etching profile (vertical sidewalls) of 40 nm pillar features.

In summary, the outstanding etch performance of UBT8/C_{60} mixture allows a very efficient cryogenic etching of very thin high resolution patterns without the need of an additional hard mask.

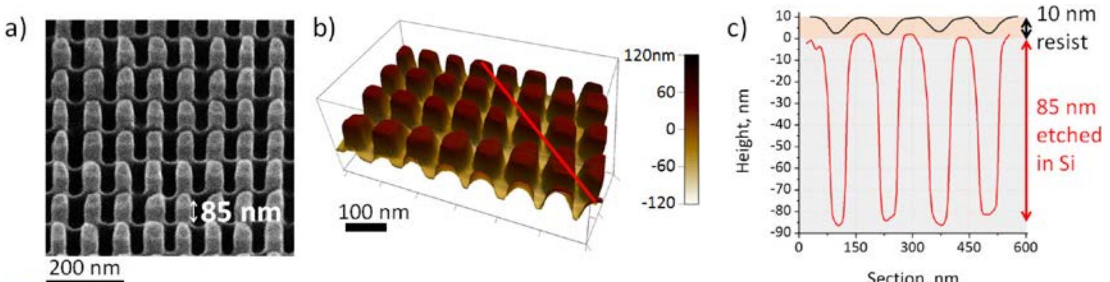


Figure 8: Cryogenic etch investigation carried out at TUIL on a 10 nm thick resist film of molecular glass mixture UBT8/C_{60}. A) SEM image of tilted pillars after cryogenic etching to demonstrate the achieved anisotropic etching (vertical sidewalls) up to a depth of 85 nm. b) and c) shows the corresponding AFM measured image with section profile.

	Conclusion The realized extensive investigations on molecular glass resists within the SNM project with respect to their thermal properties, film forming behavior, high resolution patternability by several SPL techniques, and their etch performance demonstrates that this class of resists offer distinct advantages as compared to well-known, extensively optimized, and typically used polymeric resist materials. For o-SPL at CSIC a novel molecular glass resist was developed, which offers oxidative cross-coupling by o-SPL and thus acts as a negative type resist. Here, the resolution limit is not investigated up to now, but it was observed that the molecular glass resist protects the Si surface to oxidation during the LAO process and thus allows the patterning of resist surfaces without oxidation of the Si surface. Concerning t-SPL at IBM and SL, the molecular glass of UBT12 prepared by physical vapor deposition offered high resolution features of half pitch of 11 nm without an extensive optimization, which is close to the obtained 8.9 nm high resolution pattern written in an optimized PPA stack. FN-SPL at TUIL is able to write high resolution pattern of 7.5 nm half pitch using their highly optimized standard calixarene resist CMC4R. Using the within the SNM project developed UBT8 and C_{60} mixture clear 10 nm features are demonstrated and their resolution limit is not identified yet. However, the UBT8 and C_{60} mixture can only be prepared by physical vapor deposition and shows distinct advantages in imaging of the obtained features and offers an excellent etch selectivity of more than 8:1 (Si:Resist, cryogenic etch transfer at -120°C) for feature sizes below 100 nm.
Explanation of Differences between Estimation and Realisation	The investigations within the SNM project demonstrate that molecular glass resists are alternative resist materials for the different SPL techniques. But to establish them as resist films in the running SPL processes more extensive investigations have to follow. Derivation concerning estimated PMs is given as some more PMs were invested in D5.1 (+1 PM), D5.2 (+4 PM), and D5.3 (+0.5 PM) to push WP5 from the beginning of the SNM project. In addition, OSC focused activities on WP4 + WP6 and transferred 1PM to WP6.
Metrology comments	FTIR spectroscopy was used to analyses the ongoing chemistry during the Diels-Alder reaction. AFM and SEM measurements were realized at TUIL, CSIC, and IMEC using their calibrated tools. EDX were performed at CSIC to measure the oxygen content at the Si-substrate. Layer thickness measurements were realized by a mechanical profilometer at UBT and the values given are an average out of at least three individual measurements at different positions.