Funded by
the European Union

SNM
Work Package 5
Deliverable: 5.4 (“Evaluation report about tailored molecular glass resists”)

Addendum

Additional Person-months by partner for the Addendum	OSC	UBT								
	+8.0	+1.0								

Author	• Phil Prewett and Alex Robinson	
Reviewed by:	• WP5 Leader: Christian Neuber • WPG2 Leader: Mike Cooke • Coordinator: Ivo W. Rangelow	
Criteria and Achieved Results	**Criteria of Achievement**	**Summary of Achieved Results**
	OSC novel fullerene HM-01 series resist process optimization and patternability trials using Helium ion beam lithography.	Stable process and nano-patterning limits identified in WP4, D4.5

Description of the addendum

Report of work completed on fullerene polymer resists based on mono-adduct of the C_{60} molecule as specified in the DOW. The report includes a summary of process chemistry and results of the evaluation of the resist for its application in Scanning Helium Ion Beam Lithography (SHIBL):

OSC Contribution: Negative Tone Spin Coated Fullerene Resist

Introduction

OSC’s contribution to D5.4 consisted of work on the formulation and processing of liquid spin-coatable resists based on the C_{60} molecule. The work on these fullerene resists is described in full detail in the paper *Solvent Effects in a Fullerene Resist for Scanning Helium Ion Beam Lithography,* as submitted to the journal Microelectronic Engineering and presented in full in Annexe III of deliverable D4.5. A summary of the work relevant to WP5, deliverable D5.4 is presented below. (The OSC team for this work was strengthened by the recruitment on a part time basis of Dr. Alex Robinson of Birmingham University and Irresistible Materials Ltd; total OSC staff effort expended on the deliverable was 8 pm).

A family of fullerene resists code-named HM-01 was further developed for He ion beam lithography – the chosen evaluation method. (These resists had previously been shown to

perform well in electron beam lithography). The HM-01 resist is based on a mono-adduct methanofullerene derivative. The fullerene molecule, with its 60 carbon atoms in a three dimensional cage or ring structure, gives the maximum possible ring parameter value and the minimum possible Ohnishi number. Additionally fullerene is a small molecule (<1 nm diameter), potentially compatible with lithography on the sub-10nm scale required.

Formulation

For the development of an ultra-thin film, ultra-high resolution resist for He ion beam, an easily synthesized fullerene derivative with high overall carbon content and good solubility in appropriate spin coating solvents was identified and used as the basis of the proprietary resist series HM-01 (Irresistible Materials Ltd). The structural class of the fullerene derivative is indicated in figure A1.

To synthesize the material, fullerene was added to a flask of degassed o-dichlorobenzene at a concentration of 20 g/L. To the solution was added 1 mol eq. of precursor and 1 mol eq. of an organic base. The solution was heated to 80 °C under argon and stirred while exposed to visible light. The reaction progress was monitored by HPLC and, when complete, the heat and light turned off. Upon reaching room temperature, the solution was filtered. The filtrate was purified by chromatography over silica gel using o-dichlorobenzene and toluene. The unreacted fullerene was collected first, followed by the desired product, which was subjected to rotary evaporation until concentrated, then precipitated by the addition of an excess of methanol. The mixture was filtered, and the product was dried under vacuum at 50 °C overnight.

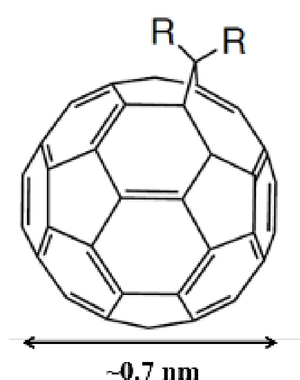


Figure A1: Schematic of a mono-adduct methanofullerene derivative.

The resultant medium-brown powder was checked for dryness by TGA (<2% residual solvent) and purity by HPLC (>99.5%). The carbon content of the material was found to be ~95 wt%; the Ohnishi parameter was ~1.26, and the ring parameter ~0.87. The resist can be formulated in various solvents, including chloroform, chlorobenzene and anisole. Chloroform was rejected as a solvent for SHIBL patterns due to poor results seen in electron beam patterning and due to its hazardous nature. Chlorobenzene and anisole are the typical solvents utilized for PMMA resist formulations, and were therefore chosen to formulate the two preferred resist versions HM-01A (anisole solvent) and HM-01C (chlorobenzene solvent). The resist was dissolved at a concentration of 5 g/l in each solvent and filtered with a 200 nm teflon syringe filter prior to spin coating. Smooth films were seen for spin speeds up to 5000 rpm. Films were apparent in the range 6000–8000 rpm but were insufficiently smooth to make an accurate thickness measurement. Films spun from anisole were on average ~15% thinner than those spun from chlorobenzene (see D4.5 Annexe III for details).

Funded by
the European Union

Evaluation

The response of the resists to helium ion beam lithography, and to electron beam lithography was evaluated at 30 kV in both cases, with cyclohexanone development. Figure A2 shows the responses of HM-01A and HM-01C after exposure to a range of doses of helium ions. The sensitivity, taken for a negative tone resist as the dose at which 50% of the film is retained after development, is 30 µC/cm^2 for the chlorobenzene solvent and 50 µC/cm^2 for the anisole solvent. The contrast for both formulations was ~3.

The electron beam response is shown for comparison in figure A3. A significantly higher dose of ~20 mC/cm^2 is required for 50% retention of the film in this case. This indicates that the HM-01A resist is between 400 and 667 times faster when exposed with helium ions, depending on the solvent used, when compared with e-beam exposure at the same beam energy.

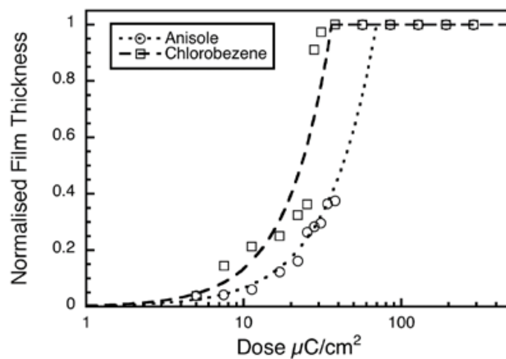


Figure A2: He ion beam dose response curve HM-01A and HM-01C.

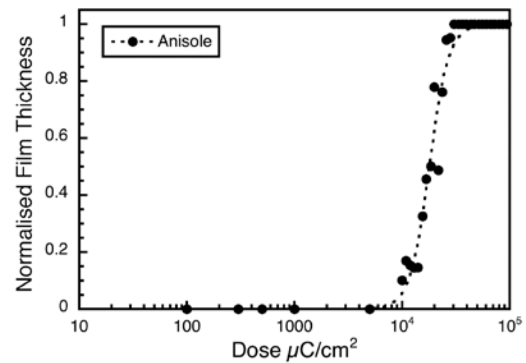
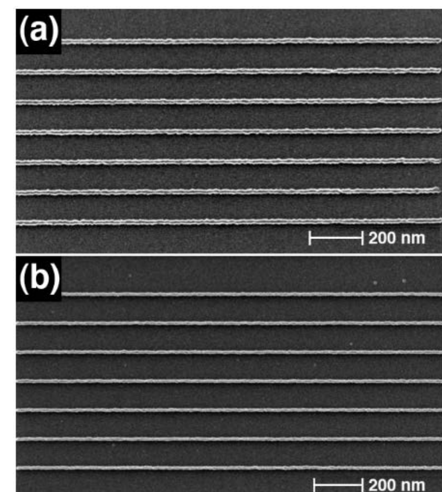


Figure A3: Electron beam dose response curve for HM-01A.

Figure A4: Isolated single pixel lines patterned by SHIBL on a pitch of 100 nm
(a) HM-01C: line dose 130 pC/cm; linewidth 12 nm
(b) HM-01A: line dose 100 pC/cm; linewidth 8 nm.



Parameter		HM-01A	HM-01C
Spun thickess		6nm/7000rpm	10nm/4500rpm
Sensitivity			
30keV	e- exposure	20mC/cm^2	
30keV	He+ exposure	50µC/cm^2	30µC/cm^2
Contrast		2.8	2.9
Etch rate		43nm/min	62nm/min

Table A1: Summary of evaluation results for HM-01 fullerene based resists.

Figure A4 shows He ion microscope images of typical sparse line patterns obtained using the two resist formulations (a) HM-01C and (b) HM-01A written at an ion beam energy of 30keV. The superior quality of the lines in HM-01A (8nm) compared with those in HM-01C is clear from the images, for the same pitch of 100 nm in each case. Etch tests carried out at IMEC showed the formulation HM-01A to have very low etch rate in CF plasma, comparable with the best of the molecular glass resists tested in the project, *viz.* 43.2nm/min (Imec in SNM 2nd Periodic Report, Figure WP6.22, 16/02/15).

A summary of the evaluation results discussed above is given in Table A1.

Conclusions

An experimental study of novel fullerene based spin-coatable resists compatible with scanning helium ion beam lithography (SHIBL) was undertaken in collaboration with Birmingham University and Irresistible Materials Ltd. The two preferred formulations, optimized in the project, were evaluated using He ion beam Lithography and electron beam lithography. The sensitivity of both resists using ion beam lithography was ~400- 600x that of the same resist using electron beam lithography at the same beam energy (30keV). Resist HM01-A demonstrated the better performance in SHIBL applications, as shown above. Elsewhere (D4.5), we report linewidths down to 7.3 nm with an ultimate resolution, limited by shot noise, of 6 nm linewidth for HM-01A. Both resists demonstrated excellent CF plasma etch resistance with HM-01A scoring better than all other resists from the project when tested at IMEC.

Explanation of Differences between Estimation and Realisation

OSC expended a total of 8 PM in staff effort, compared with an estimate of 5.5 PM. OSC effort was transferred from WP6 where demand for ALD coatings was lower than anticipated.

UBT accidentally wrote in the original report 10PM instead of 11PM.

Metrology comments

OSC used a Helium Ion Microscopy (HIM) to both write and image/measure patterns in the novel fullerene resists.