

## ELECTRON BEAM IRRADIATION OF C<sub>60</sub>(OH)<sub>10</sub>

\*S.A. JANJUA and A. ROBINSON<sup>1</sup>

Accelerator and Carbon Based Nanotechnology Laboratory, Physics Division, PINSTECH, P. O. Nilore, Islamabad, Pakistan

<sup>1</sup>School of Chemical Engineering, University of Birmingham, Edgbaston, Birmingham B15 2TT, U.K

(Received September 02, 2010 and accepted in revised form October 11, 2010)

---

The polyhydroxylated fullerene derivative, or fullerol, C<sub>60</sub>(OH)<sub>10</sub>, has been investigated as an electron beam resist. Films of fullerol of ~ 200 nm thickness, were prepared on silicon substrates using spin coating. Upon exposure with electrons at 20 keV the fullerol displayed negative tone resist behaviour after development with isopropyl alcohol:cyclohexanone (1 : 4). The fullerol became insoluble after exposure to a dose of ~ 10 mC/cm<sup>2</sup> for 20 keV electrons.

**Keywords:** E-beam lithography, Fullerol, Negative resist, Spin coating

---

### 1. Introduction

Electron beam lithography (EBL) is an important high resolution patterning technique for nanotechnology research in areas such as high-density magnetic storage and next generation electronic device fabrication [1,2]. It is typically used to fabricate devices requiring extremely small (sub 20 nm) feature sizes, for fundamental studies and in small scale prototyping where mask costs would be prohibitive. From a commercial perspective the primary use for electron beam lithography is in mask making where the ability to create arbitrary patterns is critical and in small-scale production of specialized devices [3, 4]. However, in the context of mass-produced integrated circuitry, the low throughput of electron beam lithography has significantly restricted the utility of the technique. Although the resolution of electron beam lithography far outclasses that of any other current or proposed commercial lithography system, the slow speed of the technique, due to the serial nature of EBL patterning, prevents its cost effective application except where no other alternative exists (cf mask making) [5]. Nevertheless in recent years there has been a significant resurgence of interest in novel high speed electron beam techniques, such as Multiple Aperture Pixel by Pixel Enhancement of Resolution (MAPPER) which uses numerous electron beams in parallel to speed the writing

process, and Reflective Electron Beam Lithography (REBL) which is a new form of projection electron beam lithography [6, 7].

In EBL a beam of electrons is used to modify an electron sensitive 'resist' coated on a substrate. The beam modifies the solubility of the resist so that a developing solvent can remove either the exposed or the unexposed areas (positive or negative tone respectively). The pattern recorded in the retained resist is then transferred to the substrate, for instance by etching the parts of the substrate no longer protected by resist. The properties of the resist can therefore play a key role in determining whether patterning is successful. As required feature sizes have shrunk, the performance of traditional polymer based resists has struggled to meet the requirements of electron beam lithography. In particular extremely thin films of resist are required to prevent pattern collapse at high resolution, leading to increased interest in high etch durability low molecular weight resists such as calixerene, HSQ and liquid crystalline materials [8, 9]. Tada and Kanayama [10, 11] demonstrated that the fullerene C<sub>60</sub> acted as a negative EBL resist. Fullerenes are small, carbon rich molecules, which promise high resolution and extremely good durability to fluorine based etching plasmas. However, it was not possible to create a C<sub>60</sub> film using spin coating, the technique commonly employed for resist preparation, instead requiring

\* Corresponding author : saj@pinstech.org.pk

vacuum sublimation. It was subsequently demonstrated by Robinson et al. that methano and Diels Alder derivatives of fullerene formed smooth films by spin coating, that were capable of high resolution patterning [12, 13] whilst simultaneously exhibiting improved resist properties, such as enhanced sensitivity [14] and high etch durability [15]. Subsequent use of chemical amplification led to further sensitivity improvements without sacrificing resolution [16,17]. It has also been shown that an electron beam can be used to modify the electrical conductivity of fullerene derivatives such as diazafulleroids [18] and fullerols [19] allowing the direct creation of conductive nanostructures via electron beam lithography. Interest in lithography of other classes of fullerene derivative has also increased recently [20-22].

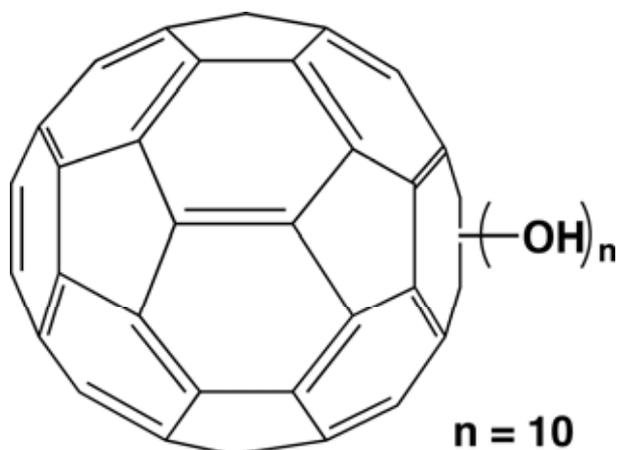


Figure 1. The polyhydroxylated fullerene, or fullerol,  $C_{60}(OH)_{10}$  used in this study.

However, whilst the fullerene derivative based resists show excellent performance as resist materials, there is concern over the use of halogenated solvents such as chloroform and chlorobenzene in the casting process and as the developer. Chen et al. proposed the use of the polyhydroxylated fullerene derivative (fullerol)  $C_{60}(OH)_{22-26}$  as an electron beam resist that could be processed using water as a solvent [23]. Here we present initial results of an investigation of the related, commercially available (Mitsubishi Corp), fullerol  $C_{60}(OH)_{10}$ , shown in Figure 1 [24].

## 2. Experimental Details and Results

Substrates were prepared from silicon <100> wafers (Rockwood Electronic Materials, n-type). In order to successfully coat the resist films it was

necessary to prepare a hydrophobic surface on the silicon. The wafers were divided into substrates of 2cm by 2cm and then cleaned ultrasonically in 2-propanol (IPA) for 10 minutes to remove dust. The substrates were rinsed in running deionised (DI) water for 1 minute, dipped in a 1:1 mixture of concentrated sulfuric acid and hydrogen peroxide for 10 minutes to remove organic contaminants, washed again in running DI water for 1 minute, followed by a 1 minute dip in a weak aqueous solution of HF, to remove the native silicon dioxide and to hydrogen-terminate the silicon, producing a hydrophobic surface. After a final 1 minute rinse in running DI water the substrates were dried with nitrogen to leave a hydrophobic surface. A hydrophobic surface was chosen because of the lack of solubility of fullerol in aqueous solvents.

A significant number of spin casting solvents and co-solvents for the  $C_{60}(OH)_{10}$  were tested, as summarized in Table 1. It can be seen that whilst a number of single solvents, such as dimethyl sulfoxide, were able to dissolve the fullerol, they were not able to form good quality spin coated films, most likely due to the low evaporation rate of the solvents. In order to prepare films it was necessary to use a co-solvent, such as 2-propanol: cyclohexanone (1:4) (IPA:CYH). Films were coated on freshly cleaned silicon substrates by depositing between 50 and 100  $\mu$ l of solution on the 2 cm by 2 cm sample and spinning at between 600 and 300 RPM for upto 340 s. In Table 1, 'no film' indicates a film of less than 5 nm thickness (the minimum that can be measured with the surface profiler); 'thin film' means thickness is less than 50 nm, which was required for good pattern transfer using electron beam lithography; 'good film' means thickness more than 100 nm.

Table 2 details example spin coating conditions and resulting film thicknesses for three of the solvents. The resulting film thickness was measured using a surface profiler (Dektak 3st Auto). The variation of film thickness across the substrate was typically 15 % or less. Subsequent testing of the  $C_{60}(OH)_{10}$  presented here was performed using samples prepared using IPA:CYH (1: 4) casting solvent.

The sensitivity of the fullerol to electrons was measured by exposing the films at 20 keV using a scanning electron microscope (SEM, FEI XL30SFEG) equipped with a pattern generator for lithography (Raith Elphy Quantum). After exposure

Table 1. C<sub>60</sub>(OH)<sub>10</sub> Casting Solvent Screening.

Solvent	Maximum Concentration (g/l)	Spin Coating Result
Chlorobenzene	0	-
Methyl Isobutyl Ketone	0	-
Chloroform	0	-
Acetone	0	-
Propylene Glycol Methyl Ether Acetate	0	-
2-Propanol	0	-
Ethanol	0	-
Methanol	0	-
$\gamma$ - Butyrolactone	0.4	No Film
2-Propanol: $\gamma$ -Butyrolactone (1:1)	0.5	Thin Film
Methanol: $\gamma$ -Butyrolactone (1:4)	0.9 <sup>a</sup>	No Film
Methanol:Cyclopentanone (1:4)	1.15	No Film
Cyclopentanone	1.7 <sup>a</sup>	Non-uniform
Dimethylformamide	2.2	No Film
Cyclohexanone	3.0 <sup>a</sup>	Non-uniform
Dimethyl Sulfoxide	7.6	Non-uniform
Methanol:Cyclohexanone (1: 2)	2.6	Thin Film
Methanol:Cyclopentanone (1: 2)	3.4	Thin Film
2-Propanol:Cyclohexanone (1: 4)	9.0	Good Film
<sup>a</sup> Insoluble residues remained, which were removed by filtration		

Table 2. C<sub>60</sub>(OH)<sub>10</sub> Film Preparation by Spin Coating.

Solvent	Concentration (g/l)	Spin Coating Conditions <sup>a</sup>		Film Thickness <sup>b</sup> (nm)
		RPM	Time (s)	
Methanol:Cyclohexanone (1:2)	2.6	1000	240	27 ± 3.2
		3000	20	
Methanol:Cyclopentanone (1:2)	3.4	600	320	24 ± 6.5
		2000	20	
2-Propanol:Cyclohexanone (1 : 4)	9.0	1000	60	214 ± 18.9
		3000	10	

<sup>a</sup> Films were formed using a two speed spin cycle. The speed was increased immediately from the first speed to the second after the indicated time (i.e without a notable acceleration ramp).

<sup>b</sup> Film thickness was measured in a number of locations using a contact surface profiler. The average is given.

the sample was immersed in IPA:CYN (1: 4) for 60 s to remove the unexposed areas and dried with nitrogen. Figure 2 shows the response of the film to electrons. The solid line represents the resist response curve and its slope indicates that it is a negative tone resist. It can be seen that a dose of

10 mC/cm<sup>2</sup> is required to expose the film (50% retention) – the same as required by pure C<sub>60</sub> [10].

In comparison, the more extensively polyhydroxylated fullerol C<sub>60</sub>(OH)<sub>22-26</sub> was previously shown to require a dose of 15 mC/cm<sup>2</sup> [23].

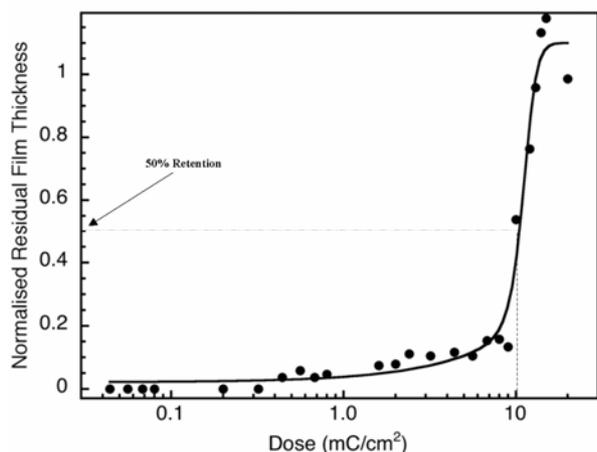


Figure 2. Response of the fullerol to irradiation with 20 keV electrons, and development in IPA:CYN (1:4) for 60 s. The residual film thickness is normalized to the pre-exposure film thickness.

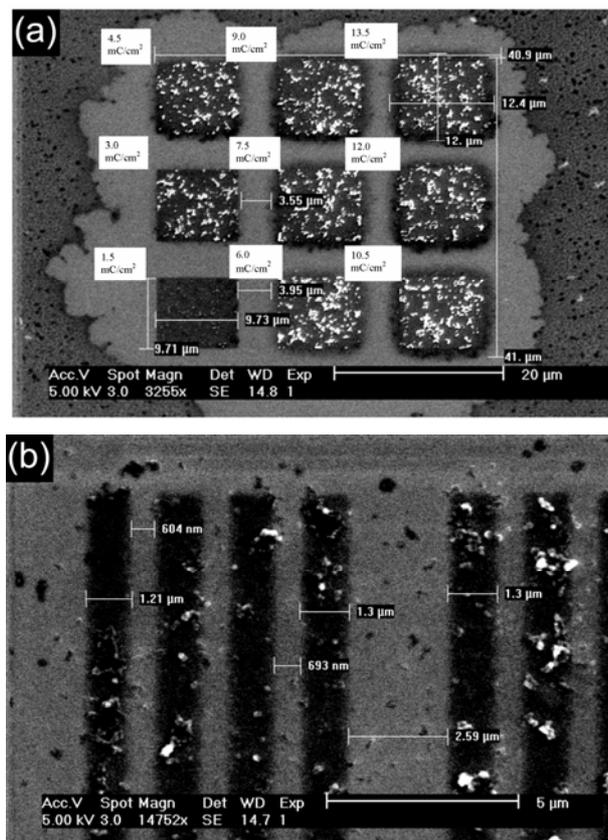


Figure 3. (a) 10 micron squares patterned at 20 keV with a dose range from 1.5 to 13.5 mC/cm<sup>2</sup> (low dose – bottom left; high dose – top right), and (b) lines and spaces on a 1 micron pitch patterned at 20 keV with a dose of 2 mC/cm<sup>2</sup>.

In order to test the resolution of the material, patterns were written using 20 keV electrons. Processing conditions were as described above. The SEM was also used to evaluate the resolution of the patterns after development. Figures 3(a) and (b) show respectively 10 µm squares patterned at doses from 1.5 to 13.5 mC/cm<sup>2</sup> and lines and spaces with a 1 µm pitch, patterned at a dose of 2 mC/cm<sup>2</sup>. Higher resolution patterns could not be achieved with this resist/casting solvent/developer combination. It can be seen from the figure that the patterned areas appear quite 'textured'. It is not clear whether this is due to aggregation of the C<sub>60</sub>(OH)<sub>10</sub> or an insoluble product of irradiation.

The resistance of the material to plasma etching was evaluated using an electron cyclotron resonance microwave plasma (ECR) etcher (Oxford Instruments, Plasmalab80+). Etching was performed at 25 °C, and a pressure of 0.001 Torr, with incident microwave power of 251 W, RF power of 17 W and SF<sub>6</sub> as the etchant. The etch rate of the fullerol to that of silicon was found to be 1/1.6 - significantly worse than that of other fullerenes studied previously, whose etch rate was typically 1/6 to 1/8 that of silicon [14].

### 3. Conclusions

In conclusion, we have shown that the fullerol C<sub>60</sub>(OH)<sub>10</sub> can be spin coated with film thicknesses of between 20 and 210 nm. It is necessary to use a co-solvent to enable spin coating, most likely due to the low evaporation rate of single component solvents for C<sub>60</sub>(OH)<sub>10</sub>. The fullerol demonstrated a negative tone electron beam resist behavior at a sensitivity similar to that of pure C<sub>60</sub>, but was not capable of high resolution patterning, and also showed significantly less etch durability than expected. The lack of resolution and durability was highly unexpected given the excellent results seen in other fullerene derivatives and may be due to the difficulty of forming high quality films and in particular the need for a co-solvent casting solution, which may have led to high levels of solvent in the cast film. More investigations can be carried out to improve films properties by trying more combination of solvents by adding surface adhesion promoters such as Hexamethyl-diisilazane, XP-0958-A PHS polymer of Shipley etc.

**References**

- [1] R.P. Cowburn and M.E. Welland, *Science* **287** (2000) 1466.
- [2] K.I. Bolotin, K.J. Sikes, Z. Jiang, M. Klima, G. Fudenberg, J. Hone, P. Kim and H.L. Stormer, *Solid State Communications* **146** (2008) 351.
- [3] H. Kawano, H. Ito, K. Mizuno, T. Matsuzaka, K. Kawasaki, N. Saitou, H. Ohta and Y. Sohda, *J. Vac. Sci. Technol.* **B21** (2003) 823.
- [4] Y. Machida, T. Maruyama, Y. Kojima, S. Sugatani, H. Tsuchikawa, K. Ogino and H. Hoshino, *Microelectronic Eng.* **87** (2010) 1131.
- [5] T. Ito and S. Okazaki, *Nature* **406** (2000) 1027.
- [6] E. Slot, M.J. Wieland, G. de Boer, P. Kruit, G.F. ten Berge, A.M.C. Houkes, R. Jager, T. van de Peut, J.J.M. Peijster, S.W.H.K. Steenbrink, T.F. Teepe, A.H.V. van Veen and B.J. Kampherbeek, *P. Soc. Photo-Opt. Inst.* **6921** (2008) 69211P.
- [7] P. Petric, C. Bevis, A. Carroll, H. Percy, M. Zywno, K. Standiford, A. Brodie, N. Bareket and L. Grella, *J. Vac. Sci. Technol.* **B27** (2009) 161.
- [8] J. Kretz, L. Dreeskornfeld, G. Ilcali, T. Lutz and W. Weber, *Microelectronic Eng.* **78-79** (2005) 479.
- [9] T. Tada, T. Kanayama, A.P.G. Robinson, R.E. Palmer, M.T. Allen, J.A. Preece and K.D.M. Harris, *Microelectronic Eng.* **53** (2000) 425.
- [10] T. Tada and T. Kanayama, *Jpn. J. Appl. Phys.* **35**, Part 2 (1996) L63.
- [11] T. Tada and T. Kanayama, *J. Photopolym. Sci. Technol.* **10** (1997) 647.
- [12] A.P.G. Robinson, R.E. Palmer, T. Tada, T. Kanayama and J.A. Preece, *Appl. Phys Lett.* **72** (1998) 1302.
- [13] X. Chen, A.P.G. Robinson, M. Manickam and J.A. Preece, *Microelectron. Eng.* **84** (2007) 1066.
- [14] A.P.G. Robinson, R.E. Palmer, T. Tada, T. Kanayama T, E.J. Shelley, D. Philp and J.A. Preece, *Mater. Res. Soc. Symp. Proc.* **548** (2000) 115.
- [15] F.P. Gibbons, A.P.G. Robinson, R.E. Palmer, M. Manickam and J.A. Preece, *Small* **2** (2006) 1003.
- [16] F.P. Gibbons, A.P.G. Robinson, S. Diegoli, M. Manickam, J.A. Preece and R.E. Palmer, *Adv. Funct. Mater.* **18** (2008) 1977.
- [17] J. Manyam, M. Manickam, J.A. Preece, R.E. Palmer and A.P.G. Robinson, *P. Soc. Photo-Opt. Inst.* **7273** (2009) 72733D.
- [18] F.P. Gibbons, M. Manickam, J.A. Preece, R.E. Palmer and A.P.G. Robinson, *Small* **5** (2009) 2750.
- [19] F.P. Gibbons, R.E. Palmer and A.P.G. Robinson, Unpublished data.
- [20] M. Wang, C-T Lee, C.L. Henderson and K.E. Gonsalves, *J. Photopolym. Sci. Technol.* **21** (2008) 747.
- [21] H. Yamamoto, T. Kozawa, S. Tagawa, T. Ando, K. Ohmori, M. Sato and J. Onodera, *P. Soc. Photo-Opt. Inst.* **6923**, (2008) 69230N.
- [22] H. Yamamoto, T. Kozawa, S. Tagawa, T. Ando, K. Ohmori, M. Sato and J. Onodera, *P. Soc. Photo-Opt. Inst.* **7639** (2010) 76390U.
- [23] X. Chen, R.E. Palmer and A.P.G. Robinson, *Nanotechnology* **19** (2008) 275308.
- [24] J-M. Zhang, W. Yang, P. He and S-Z. Zhu, *Chinese J. Chem.* **22** (2004) 1008.