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A high resolution water soluble fullerene molecular resist for electron beam lithography

X Chen, R E Palmer and A P G Robinson

Nanoscale Physics Research Laboratory, School of Physics and Astronomy, University of Birmingham, Birmingham B15 2TT, UK

E-mail: a.p.g.robinson@bham.ac.uk

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Abstract

Traditionally, many lithography resists have used hazardous, environmentally damaging or flammable chemicals as casting solvent and developer. There is now a strong drive towards processes that are safer and more environmentally friendly. We report nanometre-scale patterning of a fullerene molecular resist film with electron beam lithography, using water as casting solvent and developer. Negative tone behaviour is demonstrated after exposure and development. The sensitivity of this resist to 20 keV electrons is $1.5 \times 10^{-2} \text{ C cm}^{-2}$. Arrays of lines with a width of 30–35 nm and pitches of 200 and 400 nm, and arrays of dots with a diameter of 40 nm and a pitch of 200 nm have been patterned at 30 keV. The etch durability of this resist was found to be \~{}2 times that of a standard novolac based resist. Initial results of the chemical amplification of this material for enhanced sensitivity are also presented.

Recently, technical developments in nanofabrication have allowed the production of structures of nanometre size with many different shapes and compositions. An array of different structures, devices and systems that have novel properties and functions due to their smaller size has been generated [1–3]. One of the greatest drivers towards nanodevices has been the semiconductor industry. As lithography techniques improve, the sizes of microelectronic components have steadily decreased, whilst the performance of electronic equipment has risen. However, the increase of the performance of the traditional polymeric photoresists is struggling to keep pace with improvements elsewhere in the lithographic process and there is a growing demand for new nonpolymeric resists. The maximum allowable line width roughness is already comparable to the radius of gyration of a typical polymeric resist molecule [4, 5], and further reductions in feature size will see the required resolution itself fall below the polymer size. Furthermore, aspect ratio related pattern collapse is an increasingly common failure mode in resist films of greater than 100 nm film thickness, and thus the etch durability must be very high to allow the use of thinner resist layers.

An increasing demand for resists with higher resolution and etch durability has stimulated the development of molecular resists [6–9], including those based on fullerene resists [10–15]. These materials are promising for next generation lithography as they are small carbon rich molecules, giving the potential for higher resolution and etch durability and lower line width roughness than conventional polymeric resists. However, fullerene molecular resist films are usually prepared by spin coating from an organic solvent such as chloroform, and developed with solvents such as chlorobenzene. Current commercial photoresists are typically coated from flammable organic solvents and developed with corrosive aqueous bases. These chemicals can be difficult to handle safely, and expensive to recycle or dispose of. There is already a drive to less troublesome solvents in photolithography [16, 17], and thus the flammable nature of the solvents currently required for fullerene resists, and the fact that halogenated solvents have additional health and environmental impacts over the organic solvents normally used [18], is unwelcome.

The health and environmental hazards and the waste disposal cost associated with the use of these solvents have inspired research into water cast, water developed photoresists [16, 17, 19–21]. Taylor et al developed an...
‘all aqueous solvent’ resist with a resolution of 2.5 μm after irradiation at 366 nm [19]. Lin et al reported a chemically amplified resist system consisting of three water soluble components and achieved 1 μm features after irradiation at 248 nm and development in water [20]. Havard et al demonstrated the feasibility of a chemically amplified fully water soluble negative tone resist based on the cross-linking of a poly(vinyl alcohol) matrix resin, and also investigated films containing a photoacid together with either poly(2-isopropenyl-2-oxazoline) or poly(2-isopropenyl-2-oxazoline-costyrene) [16, 17]. As with other aqueous soluble resists, the resolution was poor, and these resists also exhibited low etch durability compared to commercial resists. Here we present the first aqueous solvent based fullerene resist. The resist utilized the commercially available (MerCorp) fullerol, shown in figure 1.

Silicon (100) wafers (Rockwood Electronic Materials, n-type) were used for all of the measurements. In order to successfully coat the resist films it was necessary to prepare a hydrophilic surface on the silicon. The wafers were divided into substrates with area 2 cm by 2 cm and then cleaned ultrasonically in isopropyl alcohol (IPA) for 10 min to remove dust. The substrates were rinsed in running deionized (DI) water for 1 min, dipped in a 1:1 mixture of concentrated sulfuric acid and hydrogen peroxide for 10 min to remove organic contaminants, washed again in running DI water for 1 min, followed by a 1 min dip in a weak aqueous solution of HF, to remove the native silicon dioxide and hydrogen terminate the silicon, producing a hydrophilic surface. The substrates were then washed in DI water again for a further minute before a second immersion in the sulfuric acid/hydrogen peroxide mixture, again for 10 min. After a final 1 min rinse in running DI water the substrates were dried with nitrogen to leave a hydrophilic surface. It should be noted that HF is itself a highly toxic acid. However, any process by which as good a quality of hydrophilic surface can be prepared could be substituted.

Fullerol solutions with concentrations in the range 20–50 g l\(^{-1}\) were prepared using DI water. It took up to 6 h (with intermittent agitation by hand) to completely dissolve the fullerol at concentrations this high, but lower concentrations were not capable of forming good films. Resist films were coated on the fresh silicon substrates by spin coating at speeds of between 500 and 2000 rpm and for up to 180 s. Between 50 and 100 μl of resist solution were typically used with the square substrates. Films with thicknesses of 20–120 nm were obtained by changing the spin conditions and or the solution concentration, as measured using a surface profiler (Dektak 3st Auto). The formation of good films relied on extremely well cleaned and fresh substrates. Addition of the surfactant aminopropyl terminated polydimethylsiloxane (up to 2% by volume) improved the film formation latitude. The maximum film thickness observed was 120 nm. Given a well-prepared substrate, good quality films were produced. The rms roughness of the films measured with the surface profiler was typically found to be up to 10% of the total film thickness. Film thicknesses, measured at several locations on the substrate with the surface profiler, were found to be constant, within the rms variation. Edge bead formation was dependent on the amount of resist solution deposited on the substrate and the spin speed, with larger quantities of solution and lower spin speeds increasing the width of the edge bead up to an observed maximum of 5 mm. Through careful selection of the spinning parameters the bead could be eliminated except at the corners of the square substrate.

The sensitivity of the fullerol resist to electrons was measured by exposing the films at 20 keV using a scanning electron microscope (SEM, FEI XL30SFEG). After exposure, the sample was immersed in DI water for 10 s to develop, and then dried using nitrogen. The film thickness prior to exposure and the retained film thickness in the exposed area after development were measured with the surface profiler, and plotted against exposure dose. The response of the resist film to electrons is shown in figure 2. From this curve we can determine the tone, the sensitivity and contrast of the resist. The sensitivity of the pure fullerol is 1.5 × 10\(^{-2}\) C cm\(^{-2}\), with a contrast of 4.8. It has previously been shown that the fullerene derivatives’ negative tone behaviour is the result of cage fragmentation, and the formation of amorphous glassy carbon [10–12]. The addition of the surfactant enhanced the sensitivity of the resist by almost an order of magnitude to 3.6 × 10\(^{-3}\) C cm\(^{-2}\) with a contrast of 2.3.

Previous aqueous solvent based resists have struggled to demonstrate high resolution patterning. High resolution patterns were fabricated using the SEM, equipped with a pattern generator for lithography (Raith Elphy Quantum).
Beam currents of between 20 and 40 pA and a beam energy of 30 keV were used for all high resolution patterning. Processing conditions were similar to those described above. The SEM was also used to evaluate the resolution of the patterns after development. Figures 3(a) and (b) show arrays of lines, with width of 30–35 nm, written with a line dose of $4 \times 10^{-5}$ C cm$^{-1}$, and pitches of 200 nm and 400 nm respectively. Some swelling is seen in the line array, evident in the slight line buckling, most likely due to the aqueous solvent [22]. This may also account for the minimum feature size of 30–35 nm. Other fullerenes using organic solvent developers have typically shown sub-20 nm resolution under similar conditions [10–15]. The patterns were analysed using IMEL Demokritos LWR software [23]. The lines in figure 3(a) show an average critical dimension (CD$_{\text{AV}}$) of 33.2 nm with a standard deviation (CD$_{\text{VAR}}$) of 2.92 nm. The line width roughness ($3\sigma_{\text{INF}}$) was 20.16 nm with a correlation length ($\xi$) of 28.1 nm and a roughness exponent ($\alpha$) of 0.53. It can be seen that the CD$_{\text{VAR}}$ is considerably less than might be expected from the $3\sigma_{\text{INF}}$ value. This is due to the swelling related buckling of the lines, which makes it difficult to establish a true value for $3\sigma_{\text{INF}}$. Dot arrays with a diameter of 40 nm and a pitch of 200 nm were achieved with a dot dose of $1 \times 10^{-15}$ C/dot, as shown in figures 3(c) and (d) at two magnifications. More complicated nanostructures were also defined. Figure 4(a) shows a grid with a pitch of 1 $\mu$m, whilst combinations of lines and closely spaced dots are shown in figures 4(b) and (c) with a minimum feature size of 38 nm. It was seen that films containing surfactant were not able to record high resolution patterns. Large area patterns were recorded, but smaller (submicron) patterns were not observed in the majority of cases, most likely due to pattern adhesion problems, as shown in figure 4(d).

In practical application, a good resist must have sufficient etch resistance for pattern transfer after exposure and development. Electron cyclotron resonance microwave plasma etching (Oxford Instruments Plasmalab 80+) was used to examine the etch durability of the resist. Etching was performed at $\sim 25^\circ$C and pressure of 0.001 Torr with incident microwave power 250 W, RF power 20 W and a DC self-bias of 123 V. The etchant was SF$_6$ at a flow rate of 6 sccm. The etch ratio of this resist after exposure and development to that of silicon is 1/5.8, while that of the commercially available high durability novolac resist SAL601 (Rohm and Haas) under the same conditions is 1/3, indicating that the fullerol resist has almost twice the durability of the novolac. The remaining fullerol resist can be stripped using an oxygen plasma, (Technics TePla 100-E Oxygen Plasma Asher). Inspection with the SEM showed no residue apparent after stripping.

Initial experiments were conducted on the chemical amplification (CA) of this resist to enhance its sensitivity. The fullerol was combined with an aqueous soluble derivative of hexamethoxymethyl melamine (HMMM, Cymel 350) crosslinker and the photoacid generator triphenylsulphonium triflate (PAG), which is also soluble in water. A ratio of 3 mg of fullerol to 0.18 mg PAG and 2 $\mu$l HMMM was used. The chemically amplified fullerol resist was coated and exposed as before. A post-exposure bake of 60$^\circ$C for 60 s was applied to the exposed CA films prior to development. Figure 5 shows the response of the chemically amplified material in comparison to the pure fullerol. The sensitivity of the amplified material is $8.5 \times 10^{-4}$ C cm$^{-2}$, with a contrast of 2.5. This represents almost two orders of magnitude of sensitivity enhancement. However, as was seen with the surfactant containing resist, it was found that high resolution was not possible with this particular formulation of the chemically amplified fullerol molecular resist, due to a combination of the adhesion problems seen with the surfactant, and anomalously high acid diffusion, as shown in figure 6, and described in more detail elsewhere for a similar fullerene based CA system [24].

Figure 3. SEM images of line arrays and dot arrays after development with deionized water. Arrays of 30 nm lines with pitches of (a) 200 nm and (b) 400 nm, and 40 nm dot arrays (c) and (d) with pitch of 200 nm and at different magnifications.
Due to the use of aqueous solvent, it has not yet been possible to identify an alternative chemical amplification scheme. It has been demonstrated that fullerol can be used as a negative tone electron resist using water as casting solvent and developer. A minimum feature size of 30–35 nm was realized using electron beam lithography. The resolution of the material is significantly better than previously reported water soluble resists, and is sufficient to address the current generation of devices [4]. Through optimization the resolution may also be able to address future nodes, but further work is required to minimize the swelling introduced by the use of water as a solvent. The sensitivity of the material is currently quite low, as is often the case for molecular resist materials. Initial testing has demonstrated that the sensitivity of the material can be significantly enhanced, to useful levels, at least in principle, by chemical amplification, but additional work on the chemical amplification is required to limit the deleterious effects of pattern adhesion loss and acid diffusion. The etch durability of this resist is roughly twice that of a conventional novolac based electron beam resist, and the material is easily removed by oxygen plasma ashing.

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References


