



CrossMark
 click for updates

Cite this: *RSC Adv.*, 2014, 4, 59817

Received 17th September 2014
 Accepted 22nd October 2014

DOI: 10.1039/c4ra10648b

www.rsc.org/advances

A hybrid polymeric material bearing a ferrocene-based pendant organometallic functionality: synthesis and applications in nanopatterning using EUV lithography†

V. S. V. Satyanarayana,^a Vikram Singh,^b Vishwanath Kalyani,^a Chullikkattil P. Pradeep,^a Satinder Sharma,^b Subrata Ghosh^{*a} and Kenneth E. Gonsalves^{*a}

Largely because of their unique physical and chemical properties, the inclusion of ferrocene derivatives into polymer backbones has attracted great attention in materials research as these hybrid organometallic polymers find wide applications in various fields. Though chemically amplified photoresists (CARs) have become the workhorses for nanopatterning in semiconductor industries, due to several inherent problems CARs cannot be used for sub 20 nm technology and therefore non-chemically amplified resists (n-CARs) are gaining attention from the photoresists community, considering their potential in patterning sub 20 nm features with good line edge roughness/line width roughness (LER/LWR) and high resolution. Given that extreme ultraviolet lithography (EUVL) is approaching well towards the commercialization phase, the present work describes the development of novel solution processable EUV-sensitive hybrid organic-organometallic polymeric non-chemically amplified photoresist materials containing pendant ferrocene units and their applications in featuring 25 nm lines and complex nanopatterns using EUVL. This resist design is accomplished by copolymers that are prepared from monomers containing sulfonium groups which are sensitive to EUV irradiation. The copolymers were characterized by ¹H NMR and IR spectroscopic techniques, gel permeation chromatography as well as thermal analyses. Whereas the photon-directed polarity change at the sulfonium center followed by scission of the polymer backbone nullified the requirement for chemical amplification, the inclusion of organometallic species in the polymer microstructure into the polymer network improved the thermal stability of the resultant hybrid system.

Since its discovery in 1951, several reports in the last few decades strongly support the great importance of the inclusion of a ferrocene functionality as a sandwiched organometallic

species into polymer backbones to tune various physical and chemical properties of base polymers.¹ Such hybrid organometallic polymers have attracted the interests of materials and applied scientists as a result of the properties required for advanced technology materials, electrical inductors and biomedical polymers.² The properties of these organometallic polymers essentially depend on the type and number of elements present, the potential for bonding with different side groups, a high abundance of inorganic elements, stability at higher temperatures, the oxidation states of metals, and much more.^{2,3}

Essentially because of their promising electrical, optical, magnetic and catalytic properties, hybrid organometallic polymers, especially ferrocene-containing polymers, find wide applications in semiconductor-supported devices.⁴⁻⁸ Moreover, research into ferrocene-containing compounds continues rapidly due to their important applications in catalysis and materials science.⁹⁻¹²

EUV light is being considered as the most viable candidate for the printing of integrated circuits using next generation lithography technology. The procedure for lithographic patterning is a series of processing steps and thus this procedure requires numerous processing parameters which interact with one another effectively. The International Technology Roadmap for Semiconductors (ITRS) provided a list of guidelines for cost-effective progresses in the performance of integrated circuits, for example, advancement of exposure tools and exposure techniques, design of integrated circuits, and closely correlated resist materials. Photoresists play a crucial role in lithographic patterning technology. Therefore, the structural engineering of photoresists by modification of the microstructures of the base polymers helps in developing photoresists with achievable lithographic CDs (critical dimensions) as well as quality patterns to be transferred to the substrate through the mask. In addition, specific photoresist system with high sensitivity to achieve features with desired characteristics from economic point of view needs to be designed according to the wavelength used in lithography technology.

^aSchool of Basic Sciences, Indian Institute of Technology Mandi, Mandi-175001, Himachal Pradesh, India. E-mail: kenneth@iitmandi.ac.in; subrata@iitmandi.ac.in

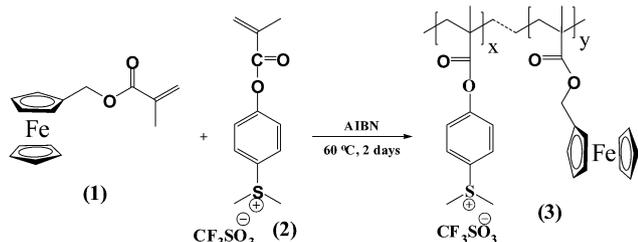
^bSchool of Computing and Electrical Engineering, Indian Institute of Technology Mandi, Mandi-175001, Himachal Pradesh, India

† Electronic supplementary information (ESI) available: Experimental procedures, spectral data and resist processing. See DOI: 10.1039/c4ra10648b

In the last few decades, several chemically amplified resists were developed in order to achieve the requirements for sub 20 nm technology using EUV lithography, but many of them are associated with several problems that include acid diffusion, low sensitivity, process complexity, post exposure instability and critical dimension (CD) control.¹³ For sub 20 nm technology, controlling the line edge roughness (LER) or line width roughness (LWR), sensitivity and resolution have become crucial, and this places an additional constraint on the chemically amplified resist (CAR).^{14,15} On the other hand, several inorganic materials have been developed over the years and used as chemically amplified photoresists for lithographic patterning with high sensitivity, better resolution and LER.^{16–21} Recently, researchers are paying attention to the development of non-chemically amplified resists (n-CARs) for sub 20 nm half pitch patterning using lithography technology to overcome the above-mentioned drawbacks of CARs. Previously, the Manners group reported the synthesis of polyferrocenylsilane-based resist materials and demonstrated them functioning as negative-tone resists in electron-beam lithography and UV-photolithography for patterning micron-sized features.^{22a} More recently, a blend of ferrocene and a commercially available photoresist has been reported as a catalytic photoresist system.^{22b} To the best of our knowledge, no efforts have been made to develop radiation-sensitive sulfonium functionality-based hybrid photoresists in which the ferrocene unit is covalently linked with the polymer backbone. In continuation of our interest in developing non-chemically amplified negative resists,²³ we wish to report a side-chain ferrocene-containing radiation-sensitive hybrid photoresist material and its application in nanopatterning using EUVL.

The monomers, (4-(methacryloyloxy)phenyl)dimethylsulfonium triflate (MAPDST) and ferrocenylmethyl methacrylate (FMMA) were synthesized following literature-reported procedures.^{24,25} The MAPDST–FMMA copolymer was synthesized by reacting MAPDST and FMMA monomers in a 90 : 10 weight ratio in the presence of AIBN (azobisisobutyronitrile) radical initiator at 1 wt% relative to the combined weight of the monomers in a mixture of tetrahydrofuran and acetonitrile (80 : 20) at 60 °C under a nitrogen atmosphere for 2 days (Scheme 1 and Table 1). The synthesized MAPDST–FMMA copolymer was obtained as a grey-colored solid. The composition of the copolymer, as determined from ¹H NMR, corresponds to a 98 : 2 ratio of MAPDST : FMMA units.

Both FTIR and NMR spectra confirmed the formation of the MAPDST–FMMA copolymer. The NMR spectra of the MAPDST–FMMA copolymer (3) is given in the ESI (Fig. S1–S3†). The



Scheme 1 Synthetic protocol of the MAPDST–FMMA copolymer.

Table 1 Polymerization results for poly(MAPDST-co-FMMA)

Monomer unit	Poly(MAPDST-co-FMMA)		Yield (%)
	Feed ratio (wt%)	Copolymer composition ^a (wt%)	
MAPDST	90	98	38.0
FMMA	10	2	

^a Compositions were calculated using ¹H NMR.

resonance peaks of all the protons of the polymer are readily assignable. The olefinic proton peaks of the MAPDST monomer disappeared in the spectrum of the MAPDST–FMMA copolymer (3). This confirms the conversion of the monomers into the polymer (see ESI†).

The peaks of the methylene (CH₂) protons present in the polymer backbone are located at δ 2.32 & 2.08 ppm, whereas the broad resonance peaks at δ 1.23, 1.30 & 1.40 ppm stem from the methyl (CH₃) protons attached to the polymer backbone. The resonance peaks at δ 3.24 ppm are assigned to the methyl (CH₃) protons attached to the sulfonium moiety and the aromatic protons of the phenyl rings are observed in the range of δ 7.44–8.06 ppm. The peak at around δ 4.73 ppm is assigned to the resonance peak of the methyleneoxy (OCH₂) protons attached to the ferrocene unit in the MAPDST–FMMA copolymer.

IR spectra of the MAPDST–FMMA copolymer exhibit absorption bands at 1753 and 1261 cm⁻¹ indicating C=O stretching and CF₃ stretching, respectively, whereas the absorption bands at 1173 and 1031 cm⁻¹ represent the presence of substituted and unsubstituted cyclopentadienyl rings bonded to iron (see ESI, Fig. S4†). The ¹³C NMR spectra of the copolymer (3) show signals at δ 174.38 and 28.41 indicating the presence of C=O and SCH₃ carbons, respectively. The carbon resonance peak for the polymeric CH₂ group attached between the MAPDST and ferrocene units at δ 45.39 indicates the formation of the copolymer (3).

The weight average molecular weight (M_w) and molecular weight distribution (M_w/M_n) of the MAPDST–FMMA copolymer was determined using gel permeation chromatography (GPC) equipped with a RI-detector (Agilent Technologies, 1260 Infinity series) using a PLGel Mixed-C column with molecular weights ranging from 5×10^2 to 5×10^5 g mol⁻¹. DMF with 1% LiBr was used as the eluent at a flow rate of 1 mL min⁻¹ at 70 °C. Poly(ethylene glycol) (PEG) and polyethylene oxide (PEO) were used as standards for the size exclusion chromatography (SEC) calibration curve. The molecular weight M_w of this newly developed poly(MAPDST-co-FMMA) copolymer was calculated to be 2.34×10^3 g mol⁻¹ with a polydispersity index of 1.23. A lower percentage (2%) of the co-monomer FMMA compared to the feed percentage (10%) in the resulting MAPDST–FMMA copolymer was possibly due to the low reactivity of the MAPDST monomer towards the ferrocene monomer (FMMA). Our previous report also witnessed low reactivity of the MAPDST monomer towards any other methyl methacrylate-based monomer compared to self-polymerization to yield a MAPDST homopolymer.^{24a}

Thermogravimetric analysis (TGA) was used to investigate the thermal stability of the polymer (Fig. 1). TGA was performed at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under an N_2 atmosphere to measure the decomposition temperature of the polymer. In TGA analyses, MAPDST-FMMA copolymer exhibited a distinct thermal transition peak in the scanning range of $20\text{ }^{\circ}\text{C}$ to $500\text{ }^{\circ}\text{C}$. The decomposition temperature of MAPDST-FMMA (3) was $239\text{ }^{\circ}\text{C}$ measured at 5% weight loss, indicating suitable thermal stability for lithographic applications.

The decomposition temperature of this hybrid system was considerably higher than the base MAPDST-homopolymer ($226\text{ }^{\circ}\text{C}$).^{24a} These experimental data indicated that the incorporation of the ferrocene unit into the polymer backbone resulted in better thermal stability of the MAPDST-FMMA hybrid compared to the MAPDST-homopolymer.

To investigate the potential of this newly developed MAPDST-FMMA hybrid resist in nanopatterning, the material was subjected to EUV lithography. The resist solution, prepared in methanol using 2% polymer by weight, was filtered through a 0.2 micron Teflon filter and spin-coated onto HMDS-treated 200 mm silicon wafers for $\sim 40\text{ nm}$ thin films, and pre-baked at $100\text{ }^{\circ}\text{C}$ for 90 s. The wafer was exposed to EUV light using a SEMATECH Berkeley Microfield Exposure (MET) tool and using mask IMO228775 with a field of R4C3 at Berkeley. First, the sensitivity was calculated from the test wafer for MAPDST-FMMA to be around 26.8 mJ cm^{-2} . After the exposure, the wafer was baked (PEB) at $115\text{ }^{\circ}\text{C}$ for 90 s, and developed in the optimized aqueous solution of tetramethylammonium hydroxide (TMAH) (0.003 N) in DI water to obtain high resolution line patterns at room temperature for 8 s. The exposed wafer was analyzed by a Nova Nano SEM 450 tool. The EUV exposure results for this non-chemically amplified MAPDST-FMMA resist at the SEMATECH-Berkeley MET lab are shown in Fig. 2 and 3. The SEM images, taken at 80 K magnification, of 25 nm high resolution lines with 25 nm CD/100 nm pitch L/3S patterns showed low LER (Fig. 2). The LER and LWR were calculated using SuMMIT® software and were found to be $3.0 \pm 2.5\text{ nm}$ and $4.2 \pm 1.3\text{ nm}$, respectively. Interestingly, complex nanopatterns were successfully printed using this hybrid material (Fig. 3). Such circular complex features have potential applications in diffraction grating.

In a recent report we explained, using EUV fragmentation studies, that the polarity change of a sulfonium functionality

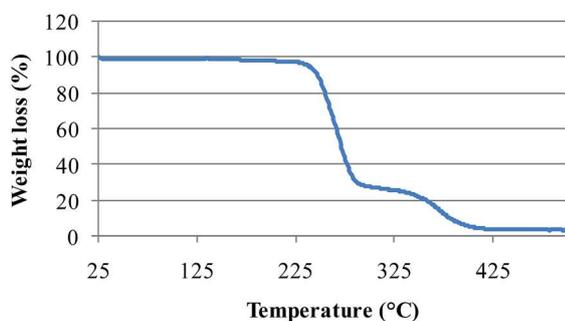


Fig. 1 TGA plot of the MAPDST-FMMA copolymer (3) at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under a N_2 atmosphere.

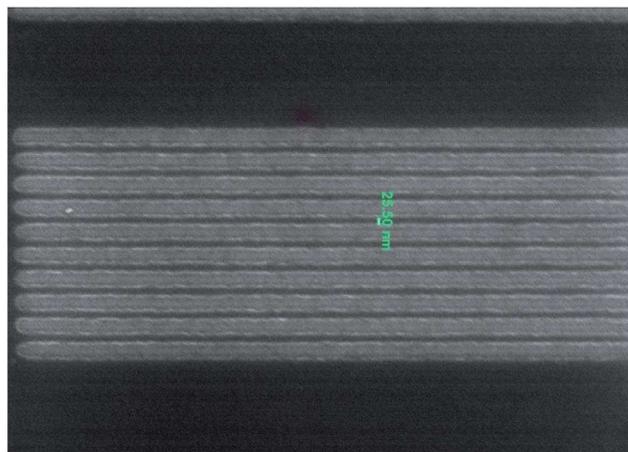


Fig. 2 High resolution EUV exposure results for 25 nm lines with L/3S patterns of the non-chemically amplified MAPDST-FMMA resist.

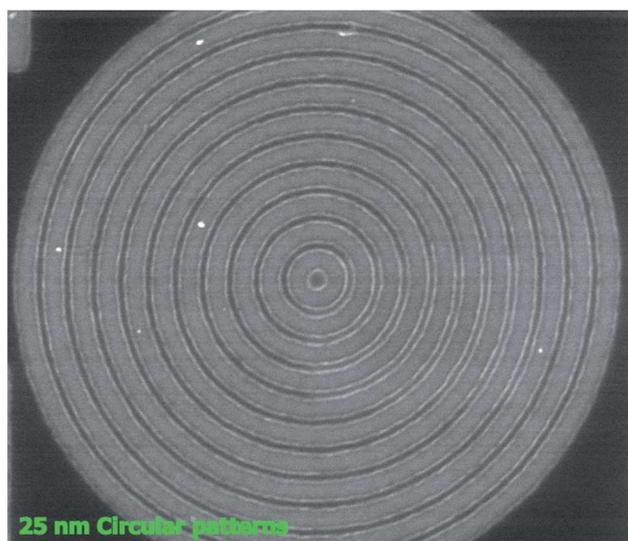


Fig. 3 EUV exposure results of the non-chemically amplified MAPDST-FMMA hybrid resist: 25 nm circular patterns.

containing photoresists upon EUV exposure is mainly due to the photodegradation of the sulfonate unit followed by polymer chain scission and charge neutralization of the sulfonium functionality through the elimination of one methyl unit, therefore producing non-polar thioether derivatives in the exposed area. These thioether derivatives ultimately become insoluble in highly polar basic aqueous developer solutions.^{24a} As the unexposed area remains highly polar, it becomes soluble in developer solutions, leaving the exposed portion intact and hence such systems act as non-chemically amplified resists.

Conclusions

To conclude, the inclusion of a ferrocene unit into the MAPDST polymer backbone as a pendant unit through covalent linkage led to the development of a structurally engineered novel hybrid organometallic copolymer resist material. This hybrid material

was found to be highly sensitive towards EUV radiation and worked as a non-chemically amplified photoresist. As expected, the incorporation of the ferrocene unit not only improved the thermal profile of the MAPDST-FMMA hybrid as compared to the base MAPDST homopolymer, but a slight improvement in its sensitivity towards EUV radiation was also observed. Furthermore, the properties of this hybrid system for application as a non-chemically amplified resist were tested using EUV lithography techniques. It was observed that the MAPDST-FMMA copolymer is capable of patterning 25 nm line features under EUV exposure conditions. Whereas the photon-directed polarity change at the sulfonium center followed by scission of the polymer backbone nullified the requirement for chemical amplification, the inclusion of an organometallic species ensured better thermal stability and efficient photon harvesting from the EUV source, resulting in enhanced sensitivity and thermal stability of the hybrid resist as compared to the pure MAPDST homopolymer resist. The present approach may pave the way for efficient hybrid n-CARs development with the incorporation of organometallic entities into the organic backbone, avoiding undesired cross-linking and thus resulting in efficient materials for semiconductor industries. More optimization studies on this hybrid material towards varying compositions of polymer microstructures and their lithographic performance, particularly patterning sub 20 nm lines, are currently under way.

Acknowledgements

Acknowledgment is made to Intel Corp USA for partial support of the project administered by SRC USA. IIT Mandi acknowledges the use of the Berkeley Microfield Exposure Tool (MET).

Notes and references

- (a) K. E. Gonsalves and M. D. Rausch, *J. Polym. Sci., Part A: Polym. Chem.*, 1986, **24**, 1599–1607; (b) K. E. Gonsalves, L. Zhan-ru and M. D. Rausch, *J. Am. Chem. Soc.*, 1984, **106**, 3863–3865; (c) J. A. Massey, K. N. Power, M. A. Winnik and I. Manners, *Adv. Mater.*, 1998, **10**, 1559–1562; (d) C. G. Hardy, L. Ren, S. Ma and C. Tang, *Chem. Commun.*, 2013, **49**, 4373–4375; (e) I. Manners, *Science*, 2001, **294**, 1664–1666.
- (a) C. E. Carraher Jr, J. E. Sheats and C. U. Pittman Jr, *Organometallic Polymers*, Academic Press, New York, 1978; (b) C. E. Carraher Jr, *J. Chem. Educ.*, 1981, **58**, 921–934; (c) A. C. Arsenault, H. Miguez, V. Kitaev, G. A. Ozin and I. Manners, *Adv. Mater.*, 2003, **15**, 503–507; (d) Z. Wang, A. R. McWilliams, C. E. B. Evans, X. Lu, S. Chung, M. A. Winnik and I. Manners, *Adv. Funct. Mater.*, 2002, **12**, 415–419.
- R. Azam, *Iran. Polym. J.*, 2004, **13**, 149–164.
- (a) A. S. Abd-El-Aziz, *Macromol. Rapid Commun.*, 2002, **23**, 995–1031; (b) M. E. Wright and E. G. Toplikar, *New Ferrocene Complexes & Polymers for Nonlinear Optical Applications*, *Advances in New Materials, Contemporary Topics in Polymer Science*, 1991.
- (a) K. Fumitoshi and A. R. David, *Annu. Rep. Prog. Chem., Sect. A: Inorg. Chem.*, 2013, **109**, 277–298; (b) W.-J. Liu, G.-X. Xiong and D.-H. Zeng, *J. Inorg. Organomet. Polym.*, 2010, **20**, 97–103.
- K. Temple, F. Jakle, A. J. Lough, J. B. Sheridan and I. Manners, *Polym. Prepr.*, 2000, **41**, 429.
- M. Refaei, L. I. Espada and M. Shadaram, *Proc. SPIE*, 2000, **4036**, 123–131.
- J. Huo, L. Wang, T. Chen, L. Deng, H. Yu and Q. Tan, *Des. Monomers Polym.*, 2007, **10**, 389–404.
- M. Herberhold, *Ferrocene Compounds Containing Heteroelements*, Wiley-VCH Verlag GmbH, Weinheim, Germany, 2007.
- A. Togni and R. L. Halterman, *Metallocenes*, Wiley-VCH Verlag GmbH, Weinheim, Germany, 1998.
- N. J. Long, *Metallocenes: An Introduction to Sandwich Complexes*, Blackwell Science, Oxford, UK, 1998.
- A. Togni and R. L. Halterman, *Metallocenes: Synthesis, Reactivity, Applications*, Wiley-VCH Verlag GmbH, Weinheim, Germany, 1998.
- J. W. Thackeray, *J. Micro/Nanolithogr., MEMS, MOEMS*, 2011, **10**, 033009.
- P. P. Naulleau, C. N. Anderson, L.-M. Baclea-an, P. Denham, S. George, K. A. Goldberg, G. Jones, B. McClinton, R. Miyakawa, S. Rekawa and N. Smith, *Proc. SPIE*, 2011, **7972**, 797202.
- W. Yayi, B. Markus, D. Wolf-Dieter, L. Antje and S. Michael, *Proc. SPIE*, 2007, **6519**, 65190R.
- Y.-J. Kwark, J.-P. Bravo-Vasquez, C. K. Ober, B. C. Heidi and H. Deng, *Proc. SPIE*, 2003, **5039**, 1204.
- T. Markos, K. Marie, S. C. Yeon, O. Christine, C. Brian, B. Robert, C. K. Ober, P. G. Emmanuel and C. Kyoungyong, *J. Photopolym. Sci. Technol.*, 2012, **25**, 583–586.
- M. Krysak, M. Trikeriotis, E. Schwartz, N. Lafferty, P. Xie, B. Smith, P. Zimmerman, W. Montgomery, E. Giannelis and C. K. Ober, *Proc. SPIE*, 2011, **7972**, 79721C.
- M. Trikeriotis, W. J. Bae, E. Schwartz, M. Krysak, N. Lafferty, P. Xie, B. Smith, P. A. Zimmerman, C. K. Ober and E. Giannelis, *Proc. SPIE*, 2010, **7639**, 76390E.
- N. Kouta, M. Ken, K. Tooru, K. Toshiyuki, G. Kentaro and S. Shalini, *Proc. SPIE*, 2011, **7969**, 79692I.
- F. Andreas, Y. Dongxu, M. Alexandra, X. Xiang, E. Yasin, E. P. Richard and A. P. G. Robinson, *J. Micro/Nanolithogr., MEMS, MOEMS*, 2013, **12**, 033010.
- (a) W. Y. Chan, S. B. Clendenning, A. Berenbaum, A. J. Lough, S. Aouba, H. E. Ruda and I. Manners, *J. Am. Chem. Soc.*, 2005, **127**, 1765–1772; (b) Y.-S. Min, E. J. Bae, J. B. Park and W. Park, *Nanotechnology*, 2006, **17**, 116–123.
- V. Singh, V. S. V. Satyanarayana, S. K. Sharma, S. Ghosh and K. E. Gonsalves, *J. Mater. Chem. C*, 2013, **2**, 2118–2122.
- (a) V. S. V. Satyanarayana, F. Kessler, V. Singh, F. R. Scheffer, D. E. Weibel, S. Ghosh and K. E. Gonsalves, *ACS Appl. Mater. Interfaces*, 2014, **6**, 4223–4232; (b) A. A. Brown, O. Azzaroni, L. M. Fidalgo and W. T. S. Huck, *Soft Matter*, 2009, **5**, 2738–2745.
- C. G. Hardy, L. Ren, T. C. Tamboue and C. Tang, *J. Polym. Sci., Part A: Polym. Chem.*, 2011, **49**, 1409–1420.