Metal-containing Polymer as Electron Beam Resist with High Resolution and High Etching Resistivity

J. Zhang, K. Cao, X. S. Wang, B. Cui,
Waterloo Institute for Nanotechnology (WIN), University of Waterloo
200 University Ave. West, Waterloo, ON, N2L 3G1,
j242zhan@uwaterloo.ca

In typical nanofabrication process using electron beam lithography (EBL), besides liftoff, dry etching is commonly carried out to transfer the nano-pattern from the resist layer to the sub-layer or the substrate. One of the most critical issues is then the etching resistance of the resist. Unfortunately, most popular resists such as PMMA, ZEP, polystyrene and SU-8 suffer from poor resistance to plasma etching. One natural solution is the incorporation of metal into the resist since metal is usually a hard mask for plasma etching. Metal has been incorporated into polystyrene or PMMA resist through co-evaporation[1] or sequential infiltration synthesis using ALD[2]. Nonetheless, synthesis of a polymer resist containing metal in its chemical structure is more desirable. Previously, metal-containing polymer, poly(ferrocenyl dimethyl silane) (PFS), was applied as a negative EBL resist, but with very poor resolution (~700 nm demonstrated)[3,4].

Here a novel iron-containing polymer, poly(cyclopenta dienyl carbonyl diphenyl phosphino acyl iron) (PFpP, see Fig. 1a), was synthesized and investigated as an electron beam resist. Electron beam exposure was carried out using Raith 150$^{\text{TWO}}$ system with 20 keV acceleration voltage. Very interestingly, it was found that this novel metal-containing polymer behaves both as positive and negative resist depending on the developer used. Fig. 2a shows the contrast curve with PFpP developed by tetrahydrofuran (THF) that is a strong solvent and dissolves the unexposed PFpP much faster than the exposed/cross-linked one, leading to the negative tone. On using a weak solvent developer, here methyl isobutyl ketone: isopropanol=1:3, the resist reversed its tone to positive as seen in Fig. 2b. High-resolution pattern with half pitch down to 20 nm and the line-width down to 17 nm was achieved by the developer of tetrahydrofuran for 1 min, shown in Fig. 1b-f.

The etching resistance to O_2 plasma (Trion RIE, 20 sccm O_2, 20 mTorr, 20 W RF power) is summarized in Table 1. As expected, the metal-containing PFpP resist demonstrated ~20× higher resistance than PMMA and ZEP resist, which is also superior to another metal-containing resist poly(sodium 4-styrenesulfonate)[5].

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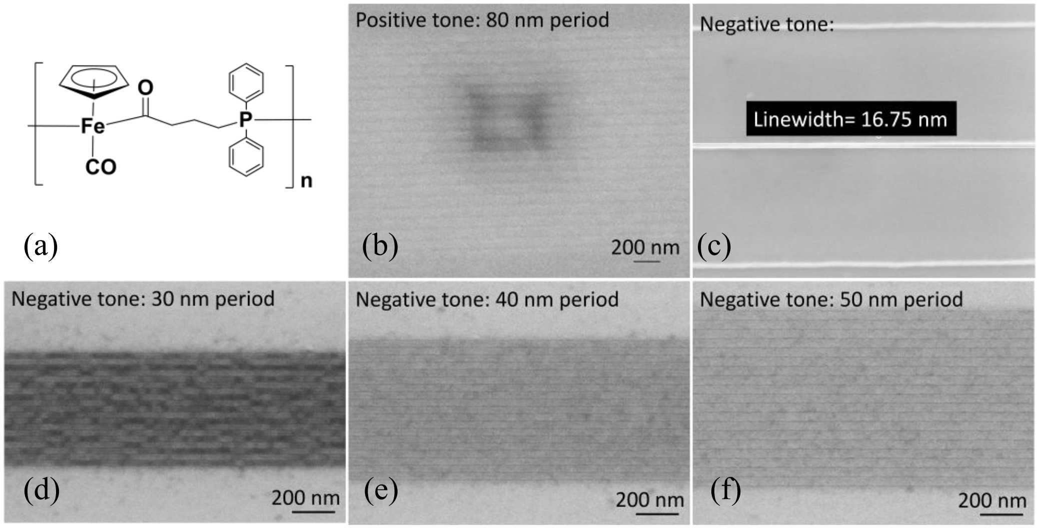

Figure 1: (a) Chemical structure of PFpP. SEM images of (b) minimum line-width of 17 nm, (c) line arrays with the period of 80 nm developed by MIBK:IPA=1:3 (positive tone), (d-f) line arrays with the period of 30 nm, 40 nm, and 50 nm, developed by THF (negative tone).

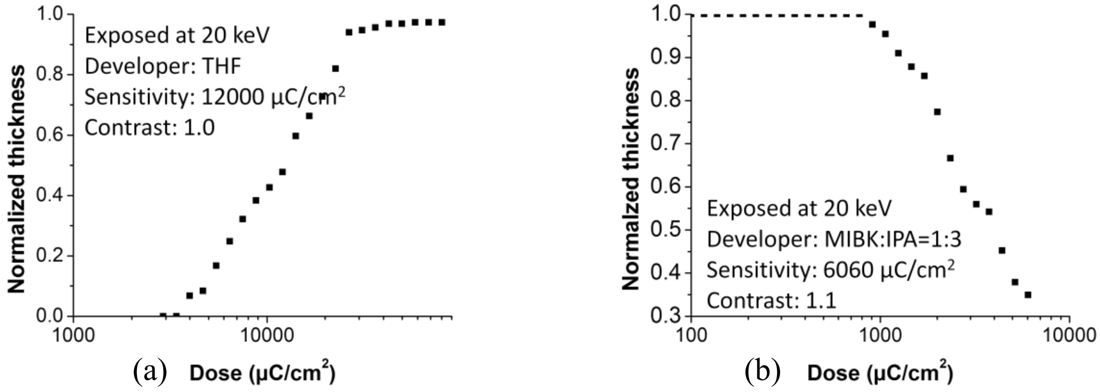

Figure 2: Contrast curve of PFpP developed by (a) THF for negative tone, and (b) MIBK:IPA=1:3 for positive tone.

RIE rate (nm/min)	PFpP	PMMA	ZEP-520A
O_2 RIE (20 sccm, 20 mTorr, 20 w RF)	8.2	200	113.4

Table 1: O_2 RIE rate of PFpP, PMMA and ZEP-520A.