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## COMMUNICATION

# Metal-Carbonyl Organometallic Polymers, PFpP, as Resists for High-Resolution Positive and Negative Electron Beam Lithography

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**Metal-containing resists for electron beam lithography (EBL) are attracting attention owing to its high dry etching resistance and possibility for directly patterning metal-containing nanostructure. The newly developed organometallic metal carbonyl polymers, PFpP, can function as EBL resist with strong etching resist. One significant feature of PFpP resist is its high resolution. Line arrays with line width as narrow as 17 nm have been created. The resist can also be used in positive tone.**

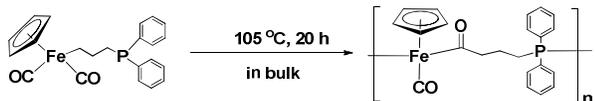
The development of synthetic chemistry for metal-containing polymers (MCPs) offers new opportunities for functional materials, such as resist material for electron beam lithography (EBL), one of the most popular nano-patterning technique for R&D and device prototyping<sup>1,2</sup>. Resistance to dry plasma etching is a very important property for EBL resist, but most organic polymer resists such as PMMA (PMMA: polymethylmethacrylate), ZEP-520A (ZEP: a commercially available high-resolution resist developed by ZEON Inc.) and PS (PS: polystyrene) do not have strong dry etching resistance<sup>3-6</sup>. To overcome this problem, thicker layer resist has been used in order to etch deep into the sub-layer. This practice usually leads to collapse of resist structures due to capillary forces. Therefore, resists with high dry etching resistance, notably metal-containing resist, is highly desired.

Various metal-containing resist systems have been previously developed<sup>7-12</sup>. First, metal can be incorporated into conventional polystyrene or PMMA resist through co-evaporation<sup>13</sup> or sequential infiltration synthesis (SIS) using atomic layer deposition (ALD)<sup>14</sup>. However, both methods rely on vacuum deposition process that is far more costly than the traditional spin-coating process. Second, metal or metal oxide nano-particles can be mixed into a polymer resist, but the resolution and line edge roughness are limited by the size of the nano-particles<sup>10</sup>. Third, metal-organic sol-gel process can be utilized to prepare the resist, but the huge volume shrinkage after

development and subsequent thermal annealing renders such resist unsuitable for patterning dense nanostructures<sup>7</sup>. Moreover, sol-gel solution is unstable and thus one has to prepare a fresh solution every time.

Apparently, chemically synthesized MCPs are advantageous to the above metal-containing resists because MCPs offer simple film preparation by spin-coating, uniform distribution of metal and long shelf life. Polyelectrolyte poly(sodium 4-styrenesulfonate) has been studied as an inexpensive and widely available negative resist, but its dry etching resistance is still low because sodium is not a hard mask against dry plasma etching<sup>15</sup>. Compared to the polyelectrolytes, it is challenging to synthesize a polymer with metal in its main chain and such kind of electron beam resist is rarely reported. Polyferrocenylsilane (PFS) and its derivatives containing Fe and Si behave as a negative resist<sup>16-18</sup> and are the only MCPs used as EBL resist for patterned nanostructure creation. However, the demonstrated resolution capability (700 nm) and sensitivity (25,000  $\mu\text{C}/\text{cm}^2$ ) are not satisfied, considering that PMMA resist can achieve 10 nm resolution and has sensitivity of 250  $\mu\text{C}/\text{cm}^2$ . Moreover, organometallic polymers as positive resists have not been reported.

PFpP is a type of newly emerged main-chain metal carbonyl MCPs with backbone constructed from both P-Fe metal coordination and Fe-C bonds<sup>19</sup>. The organometallic coordination bonds in PFpP are relatively weak compared to other organometallic polymers, e.g. PFS, which may lead to desirable resistance behavior for improved resolution. In addition, PFpP shows molecular weight-dependent solubility<sup>20</sup>. These features of PFpP prompt us to investigate into its EBL resist behavior. Preliminary results show that PFpP patterned lines with width as narrow as 17 nm can be created. Organometallic polymer resist with such high resolution has not been achieved before. We also demonstrate that, in addition to negative tone, PFpP also can be used as positive resist. The sensitivity of PFpP is similar with PFS, but much lower than organic resists.



**Scheme 1.** Synthesis of PFpCP via migration insertion polymerization.

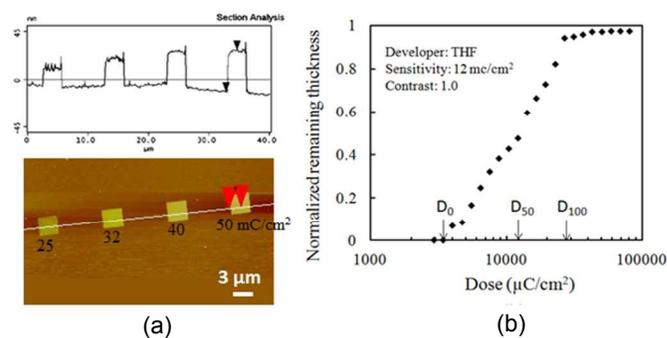
The polymer was prepared via bulk polymerization of  $\text{CpFe(CO)}_2(\text{CH}_2)_2\text{PPh}_2$  at 105 °C and characterized using IR and NMR techniques. GPC analysis reveals that the polymer has  $M_n$  of 8200 g/mol with PDI of 1.35 (supporting information). The polymer film with thickness of 60 nm was readily prepared via spin coating of PFpP solution in toluene (1 wt%).  $\text{O}_2$  RIE etching rate of the film was compared with the commonly used electron beam resists, e.g. PMMA and ZEP-520A. As shown in Table 1, the etching rate for PFpP is 8.2 nm/min, which is 24 $\times$  and 14 $\times$  slower than that for PMMA and ZEP-520A<sup>21</sup>, respectively. This comparison suggests that PFpP shows significant improvement in etching resistance. This etching resistance of PFpP is also superior to another metal-containing resist poly(sodium 4-styrenesulfonate)<sup>22</sup>. This remarkable resistance to dry etching is apparently caused by the metal content in PFpP resist. The etching rate of PFS, according to Ref 23, is 50 times slower than that for PMMA.<sup>23</sup> We therefore estimate that the etching rate of PFS under our etching condition would be 4 nm/min, which is more resistant than PFpP because both Fe and Si in PFS are resistant to oxygen plasma etching.

Table 1  $\text{O}_2$  RIE etching rate of various resist materials.

Resist	PFpP	PFS	PMMA	ZEP-520A	NaPSS
Etching rate (nm/min)	8.2	~ 4 <sup>a</sup>	200	114	10

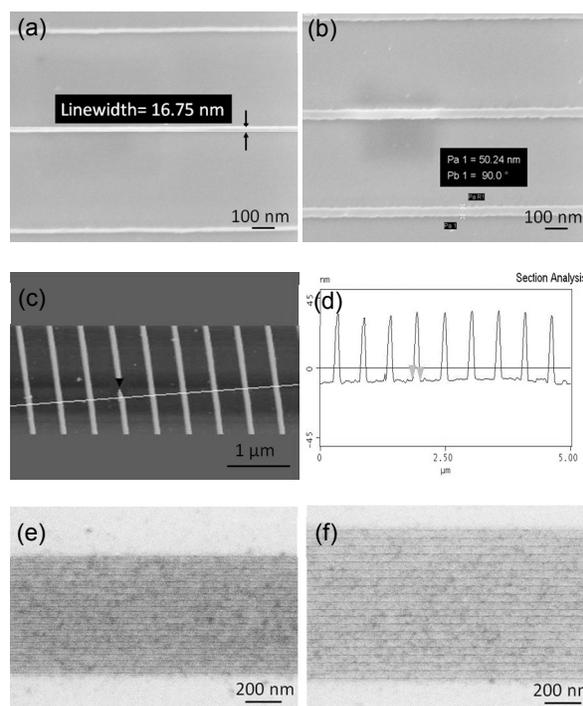
<sup>a</sup> The rate for PFS is estimated from Ref. 23.

To investigate the resist behavior of PFpP, we exposed several square patches (3  $\mu\text{m}$  by 3  $\mu\text{m}$ ) of PFpP film to electron beam with varied doses from 25,000 to 50,000  $\mu\text{C}/\text{cm}^2$ , and subsequently developed the resist using THF. As shown in Figure 1a, after the development, the exposed area became less soluble (left square) or insoluble (right square) in THF and the thickness of the remaining resists increased with the area doses (Figure 1a). This result suggests that PFpP experienced chain cross-linking upon exposure to electron beam and higher exposure dose leads to more cross-linking and less solubility. Therefore, PFpP resist has negative tone behavior. By exposing an array of squares to 20 keV electron beam with exponentially increasing doses followed by 1 min in THF for development, we obtained a contrast curve by plotting the remaining thickness against the dose (Figure 1b). The curve reveals that the “gel dose” ( $D_0$ ), minimum dose required for resist crosslink, is approximately 3,400  $\mu\text{C}/\text{cm}^2$ ; and resist sensitivity ( $D_{50}$ ), the dose required for 50% remaining thickness, is approximately 12,000  $\mu\text{C}/\text{cm}^2$ . The resist contrast, defined as  $\gamma = [\log_{10}(D_{100}/D_0)]^{-1}$  ( $D_{100}$ : dose required for 100% remaining thickness), is 1.0. These parameters are comparable to PFS,<sup>23</sup> but still much lower than those for PMMA.



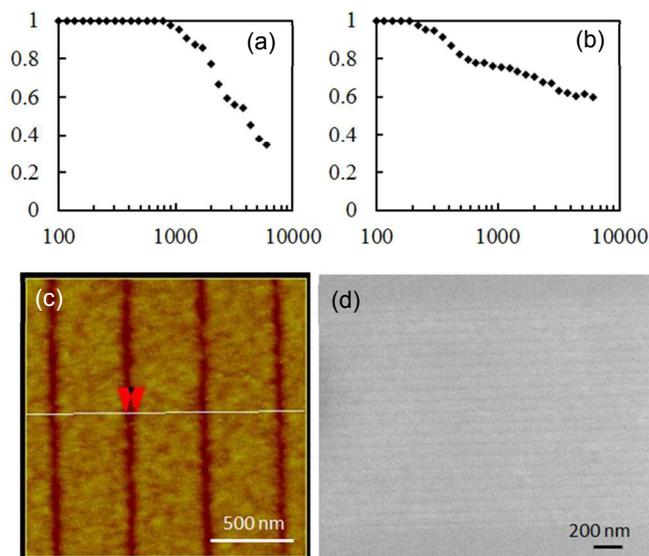
**Fig. 1** (a) Square structures obtained by electron beam exposure and development in THF. The exposure dose increases from left (25,000  $\mu\text{C}/\text{cm}^2$ ) to right (50,000  $\mu\text{C}/\text{cm}^2$ ). (b) Contrast curve of PFpP showing negative tone.

One important criterion for EBL resist is whether high structural resolution can be achieved in high density. We therefore, using PFpP as resists, developed a number of line arrays with pitch from 20 nm to 500 nm. As shown in Figure 2a, when the line array with 500 nm periods was exposed at 15 nC/cm line dose, the linewidth of 17 nm was achieved. Increasing the exposure dose to 150 nC/cm, relatively wide lines with width of 50 nm are created (Figure 2b). AFM characterization shows well aligned array with height of 45 nm, which is 15 nm thinner than the original thickness of the PFpP film (Figure 1c, d). This resolution is approaching widely used organic resist<sup>24, 25</sup> and is far superior to the previously reported PFS resist that demonstrated 700 nm feature size<sup>16, 18</sup>. Encouraged by its high resolution, we tried to produce line arrays with highly packed lines. As shown in Figure 2e, f, line array with 40 nm pitches (20 nm half-pitch) and 50 nm (25 nm half-pitch) are fairly well defined. Line doses used for these two arrays are 150 nC/cm. When we tried to push the density further down to 30 nm, the line array becomes not well defined.



**Fig. 2** SEM and AFM characterization of exposed line array patterns using PFpP resist. (a) 500 nm period, 17 nm line-width, exposed at 15 nC/cm; (b) 500 nm period, 50 nm line-width, exposed at 150 nC/cm; (c) AFM image of the array shown in (b); (d) AFM height profile showing a line height of 45 nm; (e) 40 nm period; (f) 50 nm period.

Some positive resists, such as PMMA and ZEP-520, can also be used in negative tone by increasing doses (by ca. 10 $\times$ ) of electron beam exposure<sup>26-28</sup>. This happens because, during initial exposure (low dose), the chains experience scission and the resist behaves as positive tone; upon further exposure to very high dose, the produced short chain will experience cross-linking as well as complicated carbonization process that renders the resist less soluble. We have shown that PFpP behaves as negative resist at very high exposure dose. To examine whether it can also be used as positive resist, we exposed it with low dose and developed the resist using MIBK:IPA=1:3 and amyl acetate, two popular developers (positive tone) for PMMA and ZEP-520 resists. Indeed, we found that PFpP resist can function as positive-tone resist, as evidenced by the contrast curve (Figure 3a, b) that clearly shows an increased solubility (thus reduced remaining resist thickness) with increased exposure dose. The sensitivity of PFpP resist for the positive tone is ca. 10,000  $\mu\text{C}/\text{cm}^2$ , one order lower than that for negative tone. This behavior is similar to PMMA and ZEP-520 resists. The developed line patterns with 500 nm and 80 nm periods with line dose of 30 nC/cm are illustrated in AFM and SEM images (Figure 3c, d). However, both contrast curves and the images indicate that an undesired thick residual layer remained after the development, particularly when using amyl acetate as developer. Nevertheless, the patterned lines are well resolved, confirming the possibility of using PFpP as positive resist. It is well known that the choice of right solvents as developers is a challenging issue in the study of positive tone behavior of a newly developed resist<sup>29</sup>. It is particularly the case for PFpP as a newly developed polymer, and will be continuously studied.



**Fig. 3** (a-b) Contrast curves of PFpP with positive tone behavior, developed by MIBK: IPA=1:3 for 30 s (a), and amyl acetate for 1 min (b). (c) AFM and (d) SEM image of exposed line array pattern with 80 nm period developed by MIBK:IPA=1:3.

## Conclusions

Metal carbonyl organometallic polymers, PFpPs, have been explored as electron beam lithography resist. The polymer can behave both as positive and negative electron beam resist. Due to the presence of metal atoms, the resist shows a remarkable higher resistances ( $\sim 20 \times$ ) to  $\text{O}_2$  dry etching than the organic resists, e.g. PMMA and ZEP-520A. For negative tone with THF developer, minimum line-width of 17 nm and half-pitch of 20 nm have been achieved, which is approaching the commercially available organic resists. In addition, half-pitch of 40 nm has been achieved by using PFpP resist in positive tone. The possibility for creating line arrays with high resolution and density render PFpPs promising as EML resists by taking advantage of its high beam resistance. We are working on PFpP chemistry further in an attempt to improve its resist sensitivity. The combination of high resolution and high etching resistance will be potentially useful for a deep pattern transfer, crucial from many applications, e.g. silicon photonics<sup>30</sup>.

## Notes and references

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