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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 their high dry etching resistance and possibility for directly patterning metal-containing nanostructures. The newly developed organometallic metal carbonyl polymers, PFpP, can function as EBL resists with strong etching resistance. One significant feature of the PFpP resist is its high resolution. Line arrays with line-widths 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 materials for electron beam lithography (EBL), one of the most popular nano-patterning techniques for R&D and device prototyping.[1,2] Resistance to dry plasma etching is a very important property for EBL resists, but most organic polymer resists such as PMMA (polymethylmethacrylate), ZEP-520A (ZEP: a commercially available high-resolution resist developed by ZEON Inc.) and PS (polystyrene) do not have strong dry etching resistance.[3–6] To overcome this problem, a thicker layer resist has been used in order to etch deeply into the sub-layer. This practice usually leads to the collapse of the resist structures due to capillary forces. Therefore, resists with high dry etching resistance, notably metal-containing resists, are highly desired.

Various metal-containing resist systems have been previously developed.[7–12] First, metals can be incorporated into conventional polystyrene or PMMA resists through co-evaporation[13] or sequential infiltration synthesis (SIS) using atomic layer deposition (ALD).[14] However, both of these methods rely on a vacuum deposition process that is far more costly than the traditional spin-coating process. Second, metal or metal oxide nano-particles can be mixed with a polymer resist, but the resolution and line edge roughness are limited by the size of the nano-particles.[10] Third, a 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 a resist unsuitable for patterning dense nanostructures.[7] Moreover, the sol–gel solution is unstable and thus one has to prepare a fresh solution every time.

Apparently, chemically synthesized MCPs are advantageous over the above metal-containing resists because MCPs offer simple film preparation by spin-coating, uniform distribution of the 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.[15] Compared to polyelectrolytes, it is challenging to synthesize a polymer with metals 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 negative resists[16–18] and are the only MCPs used as EBL resists for patterned nanostructure creation. However, the demonstrated resolution capability (700 nm) and sensitivity (25 000 $\mu C\ cm^{-2}$) are not satisfactory, considering that the PMMA resist can achieve 10 nm resolution and has a sensitivity of 250 $\mu C\ cm^{-2}$. Moreover, organometallic polymers as positive resists have not been reported to date.

PFpP is a type of newly emerged main-chain metal carbonyl MCPs with the backbone constructed from both P–Fe metal coordination and Fe–C bonds (Scheme 1).[19] The organometallic coordination bonds in PFpP are relatively weak compared to other organometallic polymers, *e.g.* PFS, which may lead to a desirable resistance behavior for improved resolution. In addition, PFpP shows molecular weight-dependent solubility.[20] These features of

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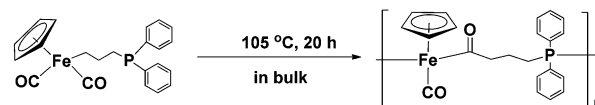
Scheme 1 Synthesis of PFpP *via* migration insertion polymerization.

PFpP prompt us to investigate its EBL resist behavior. Preliminary results show that PFpP patterned lines with a width as narrow as 17 nm can be created. An 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 a positive resist. The sensitivity of PFpP is similar to PFS, but much lower than organic resists.

The polymer was prepared via the bulk polymerization of $CpFe(CO)_2(CH_2)_3PPh_2$ at 105 °C and characterized using IR and NMR techniques. GPC analysis reveals that the polymer has an M_n of 8200 g mol^{-1} with a PDI of 1.35 (see the ESI†). A polymer film with a thickness of 60 nm was readily prepared via the spin coating of PFpP solution in toluene (1 wt%). The 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^{-1}, which is 24× and 14× slower than those of PMMA and ZEP-520A,[21] respectively. This comparison suggests that PFpP shows a significant improvement in etching resistance. This etching resistance of PFpP is also superior to another metal-containing resist poly(sodium 4-styrenesulfonate).[22] This remarkable resistance to dry etching is apparently caused by the metal content in the PFpP resist. The etching rate of PFS, according to ref. 23, is 50 times slower than that of PMMA.[23] We therefore estimate that the etching rate of PFS under our etching conditions would be 4 nm min^{-1}, which is more resistant than PFpP because both Fe and Si in PFS are resistant to oxygen plasma etching.

To investigate the resist behavior of PFpP, we exposed several square patches (3 μm by 3 μm) of the PFpP film to electron beams with varied doses of 25 000–50 000 μC cm^{-2}, and subsequently developed the resist using THF. As shown in Fig. 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 (Fig. 1a). This result suggests that PFpP experienced chain cross-linking upon exposure to the electron beam and the higher exposure dose leads to more cross-linking and less solubility. Therefore, the PFpP resist has negative tone behavior. By exposing an array of squares to a 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 (Fig. 1b). The curve reveals that the "gel dose" (D_0), the minimum dose required for resist cross-link, is approximately 3400 μC cm^{-2}, and the resist sensitivity (D_{50}), the dose required for the 50% remaining thickness, is approximately 12 000 μC 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 those of PFS,[23] but still much lower than those of PMMA.
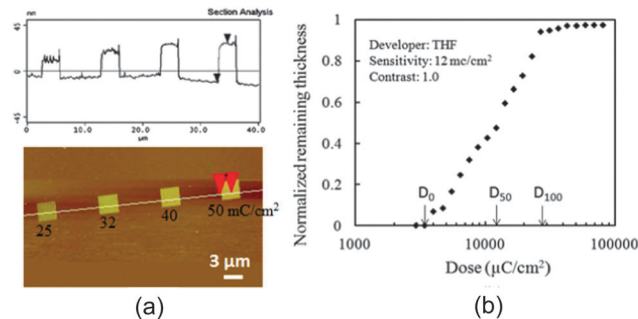

Fig. 1 (a) Square structures obtained by electron beam exposure and development in THF. The exposure dose increases from left (25 000 μC cm^{-2}) to right (50 000 μC cm^{-2}). (b) Contrast curve of PFpP showing negative tone.

One important criterion for EBL resists is whether high structural resolution can be achieved in high density. We therefore, using PFpP as resists, developed a number of line arrays with the pitch ranging from 20 to 500 nm. As shown in Fig. 2a, when the line array with 500 nm periods was exposed at the 15 nC cm^{-1} line dose, the line-width of 17 nm was achieved. Upon increasing the exposure dose to 150 nC cm^{-1}, relatively wide lines with a width of 50 nm are created (Fig. 2b). AFM characterization shows a well-aligned array with a height of 45 nm, which is 15 nm thinner than the original thickness of the PFpP film (Fig. 2c and d). This resolution is close to the resolution of the widely used organic resists[24,25] and is far
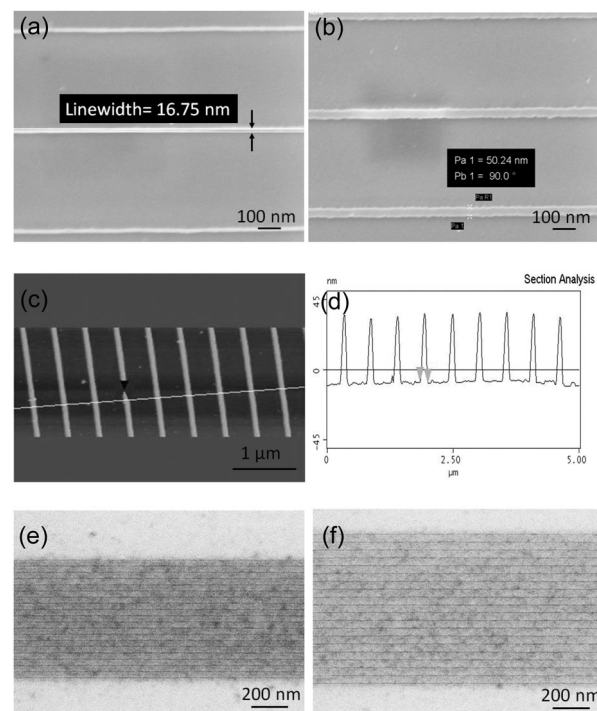

Fig. 2 SEM and AFM characterization of exposed line array patterns using PFpP resist. (a) 500 nm period, 17 nm line-width, exposed at 15 nC cm^{-1}; (b) 500 nm period, 50 nm line-width, exposed at 150 nC cm^{-1}; (c) AFM image of the array shown in (b); (d) AFM height profile showing a line height of 45 nm; (e) 40 nm period; (f) 50 nm period.

Table 1 O_2 RIE etching rate of various resist materials

Resist	PFpP	PFS	PMMA	ZEP-520A	NaPSS
Etching rate (nm min^{-1})	8.2	∼4^a	200	114	10

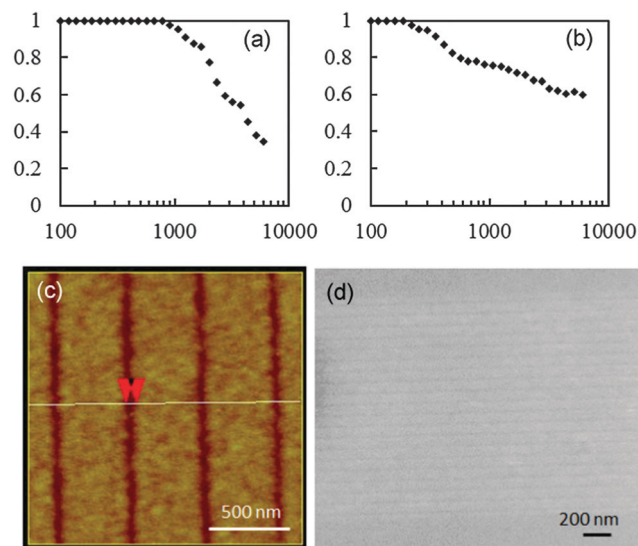^{a} The rate for PFS is estimated from ref. 23.

Fig. 3 (a and 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 images of the exposed line array pattern with 80 nm period developed by MIBK : IPA = 1 : 3.

superior to the previously reported PFS resist that demonstrated a 700 nm feature size.[16,18] Encouraged by its high resolution, we tried to produce line arrays with highly packed lines. As shown in Fig. 2e and f, line arrays with pitches of 40 nm (20 nm half-pitch) and 50 nm (25 nm half-pitch) are fairly well defined. The line dose used for these two arrays is 150 nC cm^{-1}. When we tried to push the density further down to 30 nm, the line array becomes not well defined.

Some positive resists, such as PMMA and ZEP-520, can also be used in negative tone by increasing the doses (by *ca.* 10×) of electron beam exposure.[26–28] This happens because, during the initial exposure (low dose), the chains experience scission and the resist behaves as a positive tone; upon further exposure to very high doses, the produced short chain will experience cross-linking as well as a complicated carbonization process that renders the resist less soluble. We have shown that PFpP behaves as a negative resist at very high exposure doses. To examine whether it can also be used as a positive resist, we exposed it to a low dose and developed the resist using MIBK : IPA = 1 : 3 and amyl acetate, respectively, two popular developers (positive tone) for PMMA and ZEP-520 resists. Indeed, we found that the PFpP resist can function as a positive-tone resist, as evidenced by the contrast curve (Fig. 3a and b) that clearly shows an increased solubility (thus reduced remaining resist thickness) with increased exposure dose. The sensitivity of the PFpP resist for the positive tone is *ca.* 10 000 µC cm^{-2}, one order lower than that of the negative tone. This behavior is similar to those of PMMA and ZEP-520 resists. The developed line patterns with 500 nm and 80 nm periods and a line dose of 30 nC cm^{-1} are illustrated in the AFM and SEM images (Fig. 3c and d). However, both the contrast curves and the images indicate that an undesired thick residual layer remained after the development, particularly when using amyl acetate as the

developer. Nevertheless, the patterned lines are well resolved, confirming the possibility of using PFpP as a 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.[29] It is particularly the case for PFpP as a newly developed polymer, and will be continuously studied.

Metal carbonyl organometallic polymers, PFpPs, have been explored as electron beam lithography resists. The polymer can behave as both positive and negative electron beam resists. Due to the presence of metal atoms, the resist shows remarkably higher resistance ($\sim$20×) to O$_2$ dry etching than the organic resists, *e.g.* PMMA and ZEP-520A. For negative tone with a THF developer, a minimum line-width of 17 nm and a half-pitch of 20 nm have been achieved, which is close to that of the commercially available organic resists. In addition, a half-pitch of 40 nm has been achieved by using the PFpP resist in positive tone. The possibility of creating line arrays with high resolution and density renders PFpPs promising as EBL resists by taking advantage of their 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 deep pattern transfer, crucial for many applications, *e.g.* silicon photonics.[30]

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