First-row transitional-metal oxalate resists for EUV

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Abstract. We have developed inorganic oxalate compounds $[\text{PPh}_3(\text{CH}_2\text{Ph})][\text{M}(2,2'\text{-bipyridine})_n(\text{oxalate})_{(3-n)}]$ ($n = 1, 2, 3$; $\text{M} = \text{Co}, \text{Fe}, \text{Cr}$) capable of acting as negative-tone extreme ultraviolet (EUV) resists. Two important trends are observed: (1) sensitivity increases with the number of oxalate ligands; (2) Cobalt and iron complexes exhibit greater sensitivity than analogous chromium complexes. Lithographic studies of the most successful compound, $[\text{PPh}_3(\text{CH}_2\text{Ph})][\text{Co}(2,2'\text{-bipyridine})(\text{oxalate})_2]$, show that it can consistently achieve 20 nm h/p lines at doses approaching 30 mJ/cm². Infrared, paramagnetic nuclear magnetic resonance, and cyclic voltammetric studies of this compound show that the reaction products of the EUV photochemistry are $\text{Co(II)}(2,2'\text{-bipyridine})(\text{oxalate})$ and $[\text{PPh}_3(\text{CH}_2\text{Ph})]_2(\text{oxalate})$ formed from the decomposition of one of the oxalate ligands into two equivalents each of carbon dioxide and electrons. © 2018 Society of Photo-Optical Instrumentation Engineers (SPIE) [DOI: 10.1117/JMM.17.4.043507]

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1 Introduction

For the past 8 years, the photoresist community has seen a great deal of interest in EUV photoresists containing metallic elements. This interest in metal-containing resists was probably initiated by three circumstances: (1) the ground-breaking papers by Amador et al.¹ and Chris Trikeriotis et al.² demonstrated that hafnium oxide films can act as good EUV photoresists; (2) the realization that capturing more EUV photons will be essential to provide manufacturing capabilities with the necessary photon statistics,^{3,4} and that many metals are much more absorbing than the elements (e.g., C, O, N, and F) used in conventional resists; and (3) the maturation of extreme ultraviolet lithography has convinced resist chemists to explore more exotic resist designs. Although metal contamination of integrated circuits continues to remain an open question for the industry, the exploration and discovery of new metal-based resists helps to provide indications of what is lithographically possible with these resist platforms.

Our group has evaluated the utility of creating photoresists out of 10 to 14 metals that exhibit moderate to high EUV absorptivity.^{5–10} We call this project, Molecular Organometallic Resists for EUV.

Here we present a design for EUV resists based on first-row transition-metal oxalates. Our most promising resist, $[\text{PPh}_3(\text{CH}_2\text{Ph})][\text{Co}(\text{bpy})(\text{ox})_2]$ (**NP1**), can be spin-coated to produce high-quality, amorphous films as the pure compound. Exposure to EUV followed by the development in organic solvents produce high-resolution negative-tone dense lines with good sensitivity. Infrared, nuclear magnetic resonance (NMR), and electrochemical experiments provide insight into the mechanism of photochemical reactions that occur during exposure to EUV. In particular, the electrochemical

exposures show pathways that can be initiated by reductive (e.g., electron-trapping) or oxidative (e.g., hole-initiated) reactions during EUV exposure.

Transition metal-oxalates have a well-studied history of photochemistry at longer wavelengths than EUV.^{11–13} These compounds decompose during UV–Vis photolysis by mechanisms in which the oxalate ligands are converted to CO_2 and two electrons [Eq. (1)]. The two electrons typically reduce the metal center. This reaction is potentially very useful in designing inorganic resists because the reaction is thermodynamically favorable and is simply “triggered” by a photon. Although we have explored several first-row transition metal centers in this report, we have focused on complexes containing Co(III) because they are significantly more stable toward ligand substitution than other first-row transition metal ions and because cobalt has a relatively high EUV absorptivity.

2 Results and Discussion

Here we focus on inorganic complexes of the type $\text{M}(\text{oxalate})_m(\text{bpy})_n$, where $m + n = 3$ and $\text{bpy} = 2,2'\text{-bipyridine}$. The identity of the metal was selected between Co, Cr, and Fe, and the number of oxalate ligand was varied between 0 and 3. The bipyridine ligand was chosen because it forms very stable metal–ligand bonds, is commercially available, and many derivatives can be purchased or synthesized. Figure 1 shows the compounds that have been prepared for this study.

Counter ions were selected for their ability to create soluble complexes that could be spin-coated to provide high quality coatings. We used benzyltriphenylphosphonium cation (BTP^+) in combination with the anionic metal complexes

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Compound	M =	Coating solvent	Developing solvent	Contrast curve ($E_{\max}$)
Co	1:1 AN/EL	85% 2-propanol	> 1000 mJ/cm ²
	Cr	1:1 AN/EL	85% 2-propanol	> 1000 mJ/cm ²
Co	2:1 AN/EL	95% 2-propanol	40 mJ/cm ²
	Fe	2:1 AN/EL	10% 2-propanol	n/a
	Cr	1:1 AN/EL		> 1000 mJ/cm ²
Co	1:1 AN/EL	MEK	8 mJ/cm ²
	Fe	1:2 AN/EL	1:1 Acetone:PMA	< 15 mJ/cm ²
	Cr	1:1 AN/EL		35 mJ/cm ²
Co	1:3 AN/EL	1:1 Acetone:PMA	4 mJ/cm ²

Fig. 1 Cobalt, iron, and chromium oxalate compounds prepared in this study (MEK, methyl ethyl ketone; AN, acetonitrile; and EL, ethyl lactate). Samples were spin-coated from freshly prepared solutions (2% to 3% solids) at 2000 rpm for 60 s over crosslinked polymer underlayer. Film thicknesses for contrast curves were 50 to 60 nm. Additional details about sample preparation and process are noted in the experimental. All organometallic films were exposed to at least 1000 mJ/cm² during open frame (contrast curve) exposure studies. If a sample did not show a measurable imaging response, the $E_{\max}$ value is reported as >1000 mJ/cm².

and used hexafluorophosphate anion (PF_6^-) in combination with the cationic complexes.

Contrast curves for three of these compounds are shown in Fig. 2. These all show fairly classic behavior for a negative tone resist with an approximately linear increase in film thickness with exposure dose, reaching a plateau. A range of $E_{\max}$ values for several compounds are shown in Fig. 1.

Several interesting trends in sensitivity are observed (Fig. 1). First, we see a consistent and dramatic improvement in sensitivity as the number of oxalate ligands increases from zero ($[\text{Co}(\text{bpy})_3]^{3+}$) to three ($[\text{Co}(\text{ox})_3]^{3-}$). The tris-bipyridine complex is essentially inert while the trisoxalate complex is remarkably sensitive, reaching an $E_{\max}$ at <5 mJ/cm². Additionally, the complex, $[\text{PPh}_3(\text{CH}_2\text{Ph})][\text{Co}(\text{bpy})(\text{ox})_2]$ (**NP1**), is significantly more sensitive than the analogous chromium complex.

Lithographic studies were performed at Paul Scherrer Institute (PSI) for $[\text{PPh}_3(\text{CH}_2\text{Ph})][\text{M}(\text{bpy})(\text{ox})_2]$, where M = Co(III), Fe(III), and Cr(III).¹⁴ Figure 3 shows 35-nm h/p lines for $[\text{PPh}_3(\text{CH}_2\text{Ph})][\text{M}(\text{C}_2\text{O}_4)_2(\text{bpy})]$ (M = Cr, Fe, and Co). The approximate E_{size} values are consistent with the order of sensitivity observed from their contrast curves (from best to worst: Co > Fe > Cr). This trend in

sensitivity seems to be well-correlated with the thermal decomposition temperatures of the tris-oxalates compounds of the same metals observed by Tanaka et al.¹⁵ They found that the temperature in which the oxalate decomposed for the metals Co, Fe, Cr were 120, 250, and 345°C, respectively. They attributed this trend to changes in the ease of reduction of the M(III) ion, which are generally in the order Co(III) > Fe(III) > Cr(III). This is exemplified by the reduction potentials for the $\text{M}(\text{III})_{(\text{aq})}$ ions, which are +1.92, +0.77, and -0.41 V, for $\text{Co}(\text{III})_{(\text{aq})}$, $\text{Fe}(\text{III})_{(\text{aq})}$, and $\text{Cr}(\text{III})_{(\text{aq})}$, respectively. We also note that cobalt has the highest EUV cross section and chromium has the least. As discussed in our paper on EUV optical density,¹⁶ we think that the differences in optical density between these compounds are fairly small, so we propose that the reduction potential has a stronger influence in determining their EUV photosensitivity.

The cobalt complex, $[\text{PPh}_3(\text{CH}_2\text{Ph})][\text{Co}(\text{bpy})_2(\text{ox})]$ (**NP1**), provides the best EUV imaging. This complex can image half-pitch lines down to a resolution of 22 nm with reasonable line edge roughness (LER) and dose (Fig. 4). This resist was developed with methyl ethyl ketone (MEK), which appears to dissolve away the starting material, leaving behind the relatively insoluble EUV photoproduct.

Fig. 2 Contrast curves measured by profilometry for cobalt oxalate complexes.

Fig. 3 Lithographic performance of $[PPh_3(CH_2Ph)][M(C_2O_4)_2(bpy)]$ compounds.

As Fig. 5 shows, the resist is not particularly sensitive to the development time, indicating that the solubility contrast between the starting material and photoproduct is large.

2.1 Photolysis Products of $[PPh_3(CH_2Ph)][Co(C_2O_4)_2(bpy)]$ (NP1)

It can be quite challenging to determine the solid-state products of EUV photolysis of metal-containing photoresists.^{5–10} Volatile products can typically be identified using mass-spectroscopy during exposure, but the nonvolatile products are in very thin films in quantities typically <1 mg, and no single spectroscopic technique is capable of telling the whole story.

In this section, we use visible exposure of relatively large quantities of NP1 (~200 mg) as a model for the photochemical reactions that occur during exposure to EUV light. The technique provides sufficiently large samples of photoproducts to allow for detailed analysis using IR or NMR, and allows direct comparison with authentic samples of the suspected photoproduct synthesized independently. While we recognize the very real possibility that exposure to UV–Vis light will yield different nonvolatile products than will exposure to EUV light, the wealth of information available using longer wavelengths can provide useful information about the photochemical reactions occurring at EUV, as

long as the results are interpreted with care. For both UV and EUV wavelengths, we propose that NP1 undergoes reactions specifically driven by the oxidation of oxalate to form CO₂ [Eq. (1)]. Specifically, we propose a balanced reaction for the photochemical reactions occurring with both UV and EUV, in which one molecule of NP1 produces one equivalent of CO₂, one half equivalent of the salt $(PPh_3CH_2Ph)_2(C_2O_4)$ (2), and an oligomeric, paramagnetic compound $[Co(II)(C_2O_4)(bpy)]_n$ (3) (Fig. 6). Described below are mass-spectral, infrared, and NMR data in support of this balanced reaction.

Mass-spectroscopy (EUV and e-beam). The production of CO₂ by photolysis of NP1 is consistent with the well-documented, long-wavelength photochemistry of transition metal oxalates.^{11–13} Additionally, Grzeskowiak et al.¹⁶ clearly demonstrated that the exposure of NP1 produced CO₂ as the only volatile product upon exposure to either EUV or 80 eV electrons.

Infrared spectroscopy (UV–Vis and EUV). A slurry of ~200 mg of solid NP1 in hexanes was exposed to the pyrex filtered output of a 200-W Hg vapor lamp for 6 h.¹⁷ Upon exposure to UV, the dark-red NP1 is converted to an orange powder, which we propose is a 1:1 mixture of $(BTP)_2(C_2O_4)$ (2) and $[Co(II)(C_2O_4)(bpy)]_n$ (3) (Fig. 6). Compound 3 is a known compound; therefore, we were able to synthesize it using a literature procedure. The infrared

Fig. 4 Lithographic performance of $[\text{PPh}_3(\text{CH}_2\text{Ph})][\text{M}(\text{C}_2\text{O}_4)_2(\text{bpy})]$.

Fig. 5 Development time study of $[(\text{CH}_2\text{Ph})\text{PPh}_3][\text{Co}(\text{C}_2\text{O}_4)_2(\text{bpy})]$ (NP1) with MEK; resolution = 30 nm h/p; dose = 12 mJ/cm².

spectrum of compound **3** was not a direct match to that of the orange solid mentioned above since the orange photoproduct contains both compounds **2** and **3**. However, when the orange photoproduct was washed with methanol to remove the $(\text{BTP})_2(\text{C}_2\text{O}_4)$ (**2**), the remaining solid (dark orange) produced an IR spectra, which was nearly identical to the independently synthesized compound **3** [Fig. 7(a)].

The single crystal x-ray structure of $[\text{Co}(\text{II})(\text{bpy})(\text{C}_2\text{O}_4)]_n$ (**3**) provides insight into its insolubility. The compound is a coordination polymer with oxalates bridging between adjacent $\text{Co}(\text{II})$ sites. In order to dissolve this material, a coordinating solvent is needed to break the cobalt-oxalate bonds. This structure is, therefore, consistent with NP1 acting as a negative-tone resist.

Fig. 6 Proposed balanced equation for the photolysis of **NP1** by UV and EUV light; BTP^+ , $\text{PPh}_3\text{CH}_2\text{Ph}^+$.

Fig. 7 (a) IR spectrum of a independently synthesized sample of $\text{Co}(\text{bpy})(\text{ox})$ (red) and the photoproduct of $[\text{PPh}_3(\text{CH}_2\text{Ph})][\text{M}(\text{C}_2\text{O}_4)_2(\text{bpy})]$ (blue). (b) Solid state infrared spectra of $[\text{PPh}_3(\text{CH}_2\text{Ph})][\text{Co}(\text{C}_2\text{O}_4)_2(\text{bpy})]$ and its UV-Vis and EUV photolysis products. (1) Red, before photolysis; (2) blue, after UV-Vis photolysis, and (3) green, after EUV photolysis.

Figure 7(b) shows three IR spectra in the C=O oxalate stretching region. Comparisons are made between: (1) a powder sample of **NP1** after exposure to UV and (2) a powder sample of **NP1** after exposure to UV and extraction with methanol. A third spectrum (3) was acquired by exposing a thin film (~60 nm) of **NP1** on a silicon wafer to EUV, and then acquiring the IR spectrum through the wafer. The IR of **NP1** (1) shows a complex set of vibrations, consistent with its two sets of oxalate ligands. The simple two-peak spectrum (2) of the UV-exposed and methanol-extracted sample is consistent with compound **3** since it only contains one oxalate ligand. Of particular interest is the pronounced absorption at 1615 cm^{-1} since this peak is significantly lower in energy than would be expected for an oxalate ligand coordinated in a bidentate fashion as in **NP1**.¹⁸ This low-energy absorption is characteristic of oxalate ligands that bridge between two metal centers in a tetradentate fashion as shown for compound **3** in Fig. 6.^{19–21}

Although spectrum (3) of the EUV-exposed sample is not identical to spectrum (2), it does contain a strong peak at 1615 cm^{-1} as in spectrum (2). Spectrum (3) also contains broad peaks at 1640 to 1725 cm^{-1} . We assign these broad peaks to the oxalate species in unreacted **NP1** as well as the BTP_2ox (2) salt, which should be in this film.

Paramagnetic ^1H NMR. The **NP1** visible light photo-product was analyzed using ^1H NMR without washing with methanol (Fig. 8). According to Fig. 9, this solid should contain both $[\text{Co}(\text{II})(\text{bpy})(\text{C}_2\text{O}_4)]_n$ (**3**) and salt $(\text{PPh}_3\text{CH}_2\text{Ph})_2(\text{C}_2\text{O}_4)$ (**2**). The ^1H NMR spectrum clearly shows that the four, nonequivalent protons on the bipyridine ligand have shifted dramatically from their normal chemical shift of 7.5 ppm to 15 to 100 ppm, whereas the hydrogens

Fig. 8 ^1H paramagnetic spectrum of the solid resulting from the exposure of a slurry of **NP1** in hexanes for 6 h to UV-Vis (~320 to 700 nm) light, without extraction with methanol. We propose the resulting compound will contain both the salt $(\text{PPh}_3\text{CH}_2\text{Ph})_2(\text{C}_2\text{O}_4)$ (**2**) and the oligomeric, paramagnetic compound $[\text{Co}(\text{II})(\text{C}_2\text{O}_4)(\text{bpy})]_n$ (**3**) (Fig. 9).

Fig. 9 Summary of proposed electrochemical reactions. For simplicity, the BTP cation, $\text{Ph}_3\text{PCH}_2\text{Ph}^+$, and the product salt, $(\text{Ph}_3\text{PCH}_2\text{Ph})_2(\text{C}_2\text{O}_4)$ (2) are not shown.

assigned to $(\text{PPh}_3\text{CH}_2\text{Ph})_2(\text{C}_2\text{O}_4)$ (2) have not undergone the paramagnetic shift. This ^1H NMR strongly supports the idea that both compounds 2 and 3 remain as the nonvolatile products of exposure to UV light (Fig. 9).

2.2 Electrochemical Studies

Mechanistic studies of chemically amplified EUV resists show strong evidence for the involvement of both electron trapping and hole-initiated mechanistic pathways for the photolysis of photoacid generators.²² Therefore, to gain mechanistic insight into the EUV photoreaction of NP1,

we have studied the redox chemistry of acetonitrile solutions of NP1 using cyclic voltammetry (CV). The CV of NP1 exhibits very different results when scanned in the negative direction [first reduction, then oxidation; Fig. 10(a)] or in the positive direction [first oxidation, then reduction; Fig. 10(b)]. There are four different reactions or waves, labeled (1)–(4). Reaction (3) is the only wave common to both directions.

When the scan is initiated in the negative direction [Fig. 10(a)], there is an irreversible reduction of NP1 (1) occurring at -1.5 V that we assign to the reduction of Co(III) to Co(II). It is irreversible up to 1000 mV/s. The wave (2) at -0.1 V is coupled to the -1.5 V process.

Fig. 10 Cyclic voltammograms of NP1. Both scans were collected at 200 mV/s scan rate with $0.10 \text{ M NBU}_4\text{PF}_6$ as the supporting electrolyte in acetonitrile. All potentials are relative to Fc/Fc⁺. (a) Initiated in the negative direction, (b) initiated in the positive direction, and (c) cyclic voltammogram of $[\text{PPh}_3(\text{CH}_2\text{Ph})][\text{Co}(\text{bpy})(\text{ox})_2]$. The blue trace is after 6 cycles with switching potentials of -2.2 and $+0.5$ V. The orange trace was collected after cleaning the electrode.

In other words, reaction (2) only occurs after reaction (1) has occurred. We assign reaction (2) to the irreversible oxidation of free oxalate displaced from the cobalt during the reaction that occurs at (1) by comparison to the work of Chang et al.²³

Figure 10(c) shows that the reduction wave (1) results in the formation of an insoluble product that coats the electrode. Multiple scans from 0.4 to -2.2 V cause both the reductive wave (1) and its coupled reoxidation wave (2) to disappear (blue trace). However, cleaning the electrode gives a CV that is nearly identical to the original (red trace).

A somewhat different behavior is observed when the scan is initiated in the positive direction [Fig. 10(b)]. The oxidation wave (3) common to both directions at $+1.5$ V is observed, but the reduction wave (1) originally observed in the negative direction at -1.5 V is shifted to (4) -1.9 V when going in the positive direction. We think that the oxidation reaction (3) at $+1.5$ V is the result of a cobalt-bound oxalate ligand on **NP1** undergoing a two-electron oxidation to produce two equivalents of CO_2 and the complex $[(\text{bpy})\text{Co}(\text{III})(\text{ox})]^+$ (**4**) (Fig. 9). Then compound **4** is reduced to compound **3** at -1.9 V, which then precipitates out onto the electrode resulting in the unusual appearance of the CV trace after the scan switches to the positive direction.

All of the electrochemical reactions are summarized in Fig. 9. When the CV scan is run in the negative direction with a clean electrode and pure **NP1** in solution, the one-electron reduction (1) occurs, producing the insoluble, paramagnetic compound **3** and the dissociated oxalate ligand ($\text{C}_2\text{O}_4^{2-}$). Thereafter, the free oxalate anion is oxidized during wave (2) to CO_2 . When the CV is run in the positive direction, the cobalt-bound oxalate undergoes a two-electron oxidation to produce two equivalents of CO_2 and the diamagnetic $\text{Co}(\text{III})$ complex **4** during wave (3) at $+1.5$ V. Thereafter, compound **4** is reduced to the insoluble, paramagnetic $\text{Co}(\text{II})$ complex **3**.

3 Summary

Figure 11 summarizes what we believe to be the mechanism for the photochemistry of $[\text{PPh}_3(\text{CH}_2\text{Ph})][\text{Co}(\text{bpy})(\text{ox})_2]$. In the first step, an electron is transferred from the oxalate ligand to the cobalt, reducing it from an oxidation state of III to II and forming the oxalate radical anion. This is

consistent with mechanistic studies of the photochemistry of metal oxalates in solution. In a second step, a second electron is transferred from the oxalate radical anion to a second equivalent of $[\text{Co}(\text{bpy})(\text{ox})_2]^-$, producing a second equivalent of $\text{Co}(\text{bpy})(\text{ox})$, two equivalents of $\text{CO}_2(\text{g})$, and an oxalate anion. The oxalate anion is displaced from the cobalt complex as it is reduced, as we have observed in the CV experiments. The reduction of two separate metal centers from a single oxalate has precedence from photochemical studies of $[\text{Fe}(\text{ox})_3]^{-3}$.²⁴ Not shown are the two equivalents of $\text{PPh}_3(\text{CH}_2\text{Ph})^+$ meaning that the oxalate anion will be present as the salt $[\text{PPh}_3(\text{CH}_2\text{Ph})]_2[\text{ox}]$. Although we do not directly observe this compound, we have observed that the strong match between the IR spectrum of the photoproduct and the synthesized $\text{Co}(\text{bpy})(\text{ox})$ in the oxalate stretching region only occurs after we have washed the photoproduct with methanol, suggesting that another material is present, which contains oxalate and is removed by the methanol. We also know from $^1\text{H-NMR}$ experiments that the $\text{PPh}_3(\text{CH}_2\text{Ph})^+$ remains unchanged in the photochemical reaction.

We speculate that the relatively efficient photochemistry of this system is due to the nature of how the oxalate reacts. Any reaction that involves charge separation can be stopped by simply having the charges recombine. This can be a very efficient process, particularly in the solid state. In this system, the initial transfer of an electron from oxalate to cobalt produces a very reactive oxalate radical anion that can swiftly reduce another metal center. What is likely a key subsequent step is that after the second electron transfer, two equivalents of CO_2 are formed that quickly leave the solid, making the reaction effectively irreversible. This system, overall, combines: (1) a thermodynamically unstable ligand, which is a reducing agent; (2) a metal that can be easily reduced; and (3) products that are rapidly released to prevent back reaction. We believe that these three attributes are useful in designing similar, metal-based resists.

4 Conclusions

We have demonstrated that transition metal oxalates can be used to prepare effective EUV photoresists. We believe that this is a very promising platform for continued development

Fig. 11 Proposed photochemical mechanism for the transformation that $[\text{PPh}_3(\text{CH}_2\text{Ph})][\text{Co}(\text{bpy})(\text{ox})_2]$ (**NP1**) undergoes when exposed to EUV light.

because the counterion the bipyridine ligand and/or the ligand substituents can all be altered to tune the chemical and physical properties of the resist. Given that we can already pattern sub-20-nm lines at relatively low doses, relatively small improvements could make this resist family potentially useful.

5 Experimental

General. All reagents were purchased from Sigma Aldrich or Fisher Scientific. All reagents were used as received unless otherwise specified.

Instruments. NMR spectra were obtained using a JEOL Eclipse+ 300 MHz spectrometer. All chemical shifts are reported as parts per million (ppm) relative to TMS. CV data were collected on a PAR VersaSTAT 3 potentiostat as previously described.²⁵ Potentials are referenced to ferrocene.

Compound synthesis. $\text{K}_3[\text{Co}(\text{ox})_3]$,²⁶ $\text{Na}_4[\text{Co}_2(\text{C}_2\text{O}_4)_4(\text{OH})_2] \cdot 5\text{H}_2\text{O}$,²⁷ $\text{K}[\text{Cr}(\text{bpy})(\text{ox})_2]$,²⁸ $\text{BTP}[\text{Fe}(\text{bpy})(\text{ox})_2]$,²⁹ $[\text{Co}(\text{bpy})_2(\text{ox})]\text{PF}_6$,³⁰ $[\text{Cr}(\text{bpy})_2(\text{ox})]\text{PF}_6$,³⁰ $[\text{Fe}(\text{bpy})_2(\text{ox})]\text{PF}_6$,³¹ $[\text{Co}(\text{bpy})_3](\text{PF}_6)_3$,³² $[\text{Cr}(\text{bpy})_3](\text{PF}_6)_3$,³³ $[\text{Fe}(\text{bpy})_3](\text{PF}_6)_3$,³² and $\text{Ba}[\text{Co}(\text{bpy})(\text{ox})_2]_2$ were prepared using literature procedures. Cationic complexes were metathesized to the PF_6^- salt by dissolving the chloride salt in water and adding an excess of NH_4PF_6 resulting in a precipitate, which was filtered and washed with cold water, methanol, and diethyl ether. Benzyltriphenylphosphonium salts of anionic complexes were prepared by dissolving the sodium or potassium salt in water and adding an excess of $\text{P}(\text{CH}_2\text{Ph})(\text{Ph})_3\text{Cl}$ resulting in a precipitate, which was filtered and washed with cold water, methanol, and diethyl ether.

$[\text{Co}(\text{bpy})_2(\text{ox})][\text{Co}(\text{bpy})(\text{ox})_2]$. We found the literature preparation for this compound starting with $\text{K}_3[\text{Co}(\text{ox})_3]$ to be inconsistent and developed the following procedure using $\text{Na}_4[\text{Co}_2(\text{C}_2\text{O}_4)_4(\text{OH})_2] \cdot 5\text{H}_2\text{O}$ as the cobalt source. 2,2'-bipyridine (2.66 g, 17.0 mmol) was added to 200 mL of pH = 5.5, 0.87 M acetic acid/sodium acetate buffer solution at 90°C. To this solution PbO_2 (2.55 g) was added, followed by $\text{Na}_4[\text{Co}_2(\text{C}_2\text{O}_4)_4(\text{OH})_2] \cdot 5\text{H}_2\text{O}$ (4.25 g, 5.67 mmol) and allowed to react for 12 min at 90°C. This mixture was filtered hot to remove a brown solid and the filtrate was placed in an ice bath for 2 h. The resulting purple solid was isolated by filtration, rinsed with water and acetone, and then dried.

$[\text{PPh}_3(\text{CH}_2\text{Ph})][\text{Co}(\text{bpy})(\text{ox})_2]$. $\text{Ba}[\text{Co}(\text{bpy})(\text{ox})_2]_2$ (1.5 g, 1.63 mmol) was added to a solution containing $(\text{NH}_4)_2\text{SO}_4$ (0.4932 g, 3.73 mmol) in 15 mL of water. This mixture was stirred for 30 min then filtered through diatomaceous earth in a Buchner funnel to remove the BaSO_4 . Benzyltriphenylphosphonium chloride (1.93 g, 4.96 mmol) was added to the purple filtrate and stirred with gentle heating for 30 min, cooled in an ice bath for 2 h resulting in a purple precipitate. The product was purified by recrystallization from methanol and diethyl ether yielding purple needles. Yield 33%.

Preparative scale photolysis of NP1. **NP1** (199 mg) was placed into a pyrex tube with 10 mL of hexane and a stir bar. The tube was sealed with a septum, and the solution was purged with argon. The slurry was photolysed for 6 h with the output from a 200-W Hg vapor lamp during which time the dark red of the **NP1** turned to a light orange color. The orange product was isolated by filtration, yielding 170 mg. Washing the product with cold methanol yielded a more

intensely colored orange product with the concomitant loss of about 50% of the mass.

Resist formulation and imaging. Resist formulations were made by dissolving solids in a suitable solvent at 2 to 3 wt. % solids and filtering through a 0.2- μm polytetrafluoroethylene filter. Formulations were then spin-cast onto 4-in. silicon wafers, precoated with a crosslinked underlayer (cross-linked hydroxyethyl methacrylate/methyl methacrylate copolymers). This underlayer was crosslinked during a 200°C/2 min PAB and used a thermal acid generator (King Industries) and an acid-catalyzed crosslinker. The purpose of this underlayer was to improve coating quality and adhesion. No unusual photochemical interactions between underlayer and resist were expected or observed. Except where noted, no postapplication or postexposure bakes were used because: (1) no benefits were observed when bakes were used and (2) the thermal stability of these unique thin films were unknown. Resist film thicknesses were typically 50 to 60 nm for contrast curves and ~30 nm for imaging. Unlike polymeric resists, the film thicknesses of these molecular organometallic resists are not very sensitive to spin-speeds. Instead, film thicknesses are primarily varied by changing the % solids of the compound in the resist solution. In most cases, film thicknesses were measured using profilometry.

Resist films were exposed with 13.5-nm radiation and developed with MEK for anionic compounds and alcohols, such as 2-propanol, for cationic complexes. In general, we utilize developers that clear unexposed resist films in 10 to 60 s. Two exposure tools were used for this study: the Berkeley direct contrast tool (DCT) and the PSI EUV interferometer.¹⁴ The sensitivity of the image exposures at PSI was calibrated to be as close to doses by patterning an open-source CAMP resist (OS-2)³⁴ at both facilities and correcting to the mask doses obtained at PSI to the wafer-plane doses obtained at Berkeley. All LER values were obtained from the analysis of the SEM micrographs in SuMMIT Lithography Image Analysis software.

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