Positive and Negative Lithography by Photochemical Metalorganic Deposition from Metal 2-ethylhexanoates

Simon Trudel, Guizhi Li, Xin Zhang, and Ross H. Hill*

*4D Labs and Department of Chemistry
Simon Fraser University,
8888 University Drive, Burnaby, British Columbia, V5A 1S6, Canada
* rhill@sfu.ca*

Direct, resist-free positive photolithographic deposition of various metal oxides was achieved using photochemical metalorganic deposition. The metalorganic precursors, manganese(II) 2-ethylhexanoate, nickel(II) 2-ethylhexanoate and molybdenum(II) 2-ethylhexanoate and mixtures of barium(II) 2-ethylhexanoate and titanium(IV) di-*n*-butoxide bis(2-ethylhexanoate), were all spin cast as amorphous thin films from solutions. Upon exposure to ultraviolet light, the organic components of the precursor are ejected from the film and the remaining metal is ultimately converted to amorphous metal oxide or mixed metal oxide. The photochemistry of the decomposition reaction of all precursors was monitored by Fourier transform infrared spectroscopy. Upon exposure to UV light irradiation, negative photolithography was observed. However, after a short period of exposure to UV light, positive pattern of the precursor can be developed. When this process is followed by a blanket exposure, the net result is the positive lithographic deposition of the metal oxide. By using these precursors and contact photolithography, the deposition of micron sized features of amorphous manganese, nickel and molybdenum oxide, and $\text{Ba}_{1.13}\text{Ti}_{0.17}\text{O}$ was achieved, in both the negative and positive lithography methods.

Keyword: photochemical metalorganic deposition, positive and negative photolithography, metal oxides

1. Introduction

In this manuscript we report on our efforts to extend photochemical metal organic deposition (PMOD) from an exclusively negative process to a process where both positive and negative patterns may be deposited from a single precursor. In normal lithography, a pattern is transferred from a mask to a resist and then from the resist to the material [1]. The choice of positive or negative deposition is a result of the choice of resist and developing conditions. In contrast PMOD does not utilize a resist instead of relying upon the choice of precursor and irradiation conditions to convert the exposed regions of the precursor to the desired material.

Since PMOD is a direct deposition process, it requires one less image transfer step than standard lithography. While, in theory, this will result in a higher image quality, the degree of optimization of the resist based systems is so high that this advantage will not be realized in the short term. In the shorter term, there is the advantage that is readily adapted to systems, where there is difficulty finding an appropriate etch, or where the deposition of the desired material by other methods has not been optimized.

The choice of precursors is of paramount importance in PMOD. Metal carboxylates $\text{M}(\text{OOCR})_x$, where R is a long hydrocarbon chain, have proven to be a convenient family of precursors for the deposition of metal and

mixed metal oxides[2-6]. It is believed that the photochemical reaction results in the loss of ligands to form metals, which are then oxidized in the presence of air. The resultant metal oxide is less soluble than the original precursor, hence negative lithography is normally observed.

Here we explore the possibility of using PMOD for positive PMOD. We present results investigating the mechanism of image formation and demonstrate positive lithography for a selection of metal oxide films. We use a selection of transition metal 2-ethylhexanoates for this study [7].

2. Experimental

2.1. Materials and Instruments

All manipulations of the precursors were carried under yellow filtered light, to avoid degradation from ambient lighting. Molybdenum(II) 2-ethylhexanoate in excess 2-ethylhexanoic acid (nominally 6% Mo by weight), manganese(II) 2-ethylhexanoate in mineral spirits (nominally 6% Mn by weight), and nickel(II) 2-ethylhexanoate in excess 2-ethylhexanoic acid (nominally 13% Ni by weight) were purchased from Strem. Barium(II) 2-ethylhexanoate (98%) was purchased from Aldrich. The preparation of titanium (IV) di-*n*-butoxide bis(2-ethylhexanoate) is described elsewhere [8]. Silicon(100) wafers were acquired from Wafer Net Inc., and cut and washed in-house.

Unless noted otherwise, the light UV source used for exposure of the samples was a low-pressure mercury lamp purchased from Entela.

Fourier transform infrared (FTIR) spectra were acquired using a Bomem 120 spectrometer operating at a spectral resolution of 4 cm⁻¹. The chamber of the instrument was maintained under a nitrogen atmosphere. All spectra were referenced to a clean, blank Si(100) chip, and corrected for fluctuations in the atmosphere.

Auger electron spectra were acquired using a PHI double-pass CMA, operating at a resolution of 0.85 eV. The system operated at a base pressure of 3 x 10⁻⁹ torr. Impinging electrons were extracted from a LaB₆ source and accelerated to an energy of 3 keV. Argon ion sputtering was used to clean the surface of the films.

X-ray diffraction patterns were collected using a Rigaku R-Axis RAPID-S diffractometer equipped with a Cu K_α source and an image plate area detector.

Photolithographic deposition was carried using a chromium mask on a quartz substrate. The light source for these experiments was either of an Oriel mercury/argon pencil calibration lamp, or the low-pressure mercury lamp mentioned above.

Scanning electron micrographs were acquired using a FEI 235 Dual Beam Strata scanning electron microscope equipped with a field emission electron gun and an EDAX energy dispersive spectroscopy unit.

2.2. Photolysis of the complexes

A sample of molybdenum(II) 2-ethylhexanoate (293 mg) in excess ligand was dissolved in hexane (1456 mg). This solution was filtered through a 0.22 μm filter. The surface of a 1.5 x 1.5 cm Si(100) chip was spin coated with this solution at a speed of 4000 rpm. This sample was loaded in the chamber of the FTIR spectrometer and a spectrum was recorded. The sample was irradiated with a hand-held mercury lamp (30.7 mW / cm²) for 30 seconds, and another spectrum was recorded. This process was repeated for accumulated exposure times of 0, 1, 1.5, 2, 3, 5, 7, 10, 15, 25, 35, and 45 minutes.

A similar experiment was conducted except the sample was covered with a second silicon chip as a control to measure any potential thermal reaction.

Similar samples were prepared and photolyzed such that the surface could be investigated by both Auger electron spectroscopy and XRD. These were indicative of the products found for negative lithography.

Similar samples were prepared and half of the chip covered and the surface exposed. The resultant film was rinsed with ethanol, and subsequently subjected to exhaustive photolysis. The result was then analyzed by Auger electron spectroscopy and XRD.

The photochemical and dark reactions of films of nickel (II) 2-ethylhexanoate, manganese (II) 2-ethylhexanoate, and barium (II) 2-ethylhexanoate and titanium (IV) di-*n*-butoxide bis(2-ethylhexanoate) were

studied in a similar fashion.

For lithographic experiments, the relevant solvents used for development and coating are given in the text.

2.3. Lithography

A film of molybdenum (II) 2-ethylhexanoate on a silicon (100) chip was prepared as above, except the sample was allowed to spin for 5 minutes. The film was covered by a chromium on quartz photomask. The sample was exposed for 5 minutes to UV light, using a mercury/argon pencil lamp.

The unexposed molybdenum(II) 2-ethylhexanoate precursor was removed by spin-developing, using hexane as the developer, generating a negative pattern.

In a similar experiment, the exposed sample was developed by dipping the exposed silicon chip in anhydrous ethanol for ~4 seconds. A positive image (of molybdenum(II) 2-ethylhexanoate) was obtained. This was converted to molybdenum oxide by blanket exposure by UV light.

Optical and SEM images of the samples were collected. Secondary electron images were acquired at an acceleration voltage of 10 kV, unless otherwise noted.

Similar experiments were conducted on the 2-ethylhexanoate complexes of manganese and nickel to yield both positive and negative pattern.

Similar experiments were conducted on a film, prepared by spin coating a solution containing barium (II) 2-ethylhexanoate (0.1101 g) and titanium(IV) di-*n*-butoxide bis(2-ethylhexanoate) (0.0573 g) in ethanol (0.8335 g)/hexane (0.4966 g). In this case the sample was exposed with the low-pressure mercury lamp for 8 minutes. The samples were then spin-developed by hexane, or immersion developed in distilled water for seconds yielding the negative and positive images, respectively.

Figure 1. FTIR spectra of a molybdenum(II) 2-ethylhexanoate thin film on Si(100) exposed to UV light for 0, 0.5, 1, 1.5, 2, 3, 5, 7, 10, 15, 25, 35, and 45 minutes.

3. Results

3.1. Photolysis of the Precursors

A thin film of molybdenum (II) 2-ethylhexanoate was prepared and the FTIR spectrum obtained. The region of the spectrum associated with the carboxylate ligands is shown in Figure 1. An intense band and shoulder at 1709 and 1741 cm^{-1} arise from the presence of excess 2-ethylhexanoic acid in the film. The intense absorption bands at 1530 (weakly split), 1462 and 1426 cm^{-1} are associated with the antisymmetric and symmetric C-O stretches of the carboxylate ligands. These may be assigned as previously published for related compounds [6]. The difference in energy between the antisymmetric and symmetric C-O stretches are indicative of the nature of the bonding mode of the carboxylate ligands. The difference observed here of 68 and 104 cm^{-1} is indicative of bidentate carboxylates [9].

The thin film was then exposed for 30 seconds and the spectrum recorded, Figure 1. The intensity of the bands associated with the excess 2-ethylhexanoic acid decreased in a proportion far greater than all other bands. The bands associated with the coordinated carboxylate C-O stretches also decrease.

Further irradiation leads to further loss of intensity of the bands associated with the coordinated carboxylate. These bands decreased in intensity in approximately a constant ratio. After 45 minutes of exposure, all bands associated with the complex are substantially lost. No spectral evidence for the presence of an intermediate is found during this reaction.

Control experiments, where films were not exposed with light, confirmed the photochemical nature of the reaction.

These results are consistent with the exposure leading to a ligand to metal charge transfer (LMCT) transition and consequent photoreduction of the metal [10, 11]. This results in the extrusion of carbon dioxide and the formation of a molybdenum (I) 2-ethylhexanoate and a 3-heptyl radical (Scheme 1A). The molybdenum (I) 2-ethylhexanoate is not expected to be stable and is expected to decompose yielding molybdenum along with an additional equivalent each of carbon dioxide and the 3-heptyl radical (Scheme 1B).

Scheme 1. General reactions leading to the photochemical deposition of molybdenum oxide from molybdenum(II) 2-ethylhexanoate.

The photoproduct carbon dioxide diffuses from the film. The 3-heptyl radicals undergo a bimolecular hydrogen exchange reaction yielding heptane and 2-heptene (Scheme 1C). The heptane and heptene are lost from the film by diffusion.

The films formed in this manner were then analysed by Auger electron spectroscopy. The atomic ratios were obtained from the relative intensities of the O *KLL*, C *KLL*, and molybdenum *MNN* transitions.

The surface consisted of molybdenum, oxygen and carbon. The surface was cleaned by exposure to argon ions for 30 seconds. The resultant surface was composed of Mo (22%) and O (78%). This result is consistent with the formation of MoO_3 although the determination of the extent oxidation is approximate due to the effect of sputtering. The results are summarized in Table 1 as the negative lithography result.

A similar experiment was done where half the sample was covered with a silicon chip prior to exposure. The chip was then removed and the surface developed with ethanol. The development resulted in removal of the film from the exposed region. The remaining film was subjected to blanket exposure and the resultant films analyzed by Auger electron spectroscopy. The resultant surface, after cleaning by sputtering, is composed of 26% molybdenum and 74% oxygen. The results are summarized in Table 1 as positive lithography. This material is not significantly different from the material produced in the negative deposition process.

Similar experiments were conducted with the nickel(II) 2-ethylhexanoate precursor. The spectrum of this complex is similar to the molybdenum complex except the high energy band is split into two components at 1614 and 1588 cm^{-1} . This difference is indicative of the

Table 1. Surface analysis of thin films deposited by the photodecomposition of M(II) 2-ethylhexanoate

M	Lithography Method	Sputter Time (sec)	%M	%O	%C
Mo	Negative	0	9	76	15
		30	22	78	0
	Positive	0	14	67	19
		30	26	74	0
Mn	Negative*	15	34	43	22
		30	49	51	0
	Positive	0	36	49	15
		30	49	51	0
Ni	Negative**	0	36	31	33
		60	65	7	28
	Positive**	0	34	31	35
		45	65	7	28

* from ref. 2 ** Cl impurity also observed

presence of bridging carboxylate groups [9], suggestive within this that the sample is polymerized. Similar results have been found previously [2, 4-6].

The spectral changes associated with the photolysis of this complex are shown in Figure 2. This result differed from the molybdenum complex in that an intermediate is clearly evident in the spectra of this complex. Photolysis of the film led to loss of the intense bands associated with the symmetric and antisymmetric C-O stretches but here is also evident an absorption band at 1570 cm^{-1} . This band increases in intensity and subsequently decreases during the photolysis. It is also evident from the temporal behaviour of the absorption bands that the absorption band at 1570 cm^{-1} is also associated with absorption bands in the region of 1425 and 1460 cm^{-1} .

A similar behaviour has been reported previously in the spectra obtained during the photolysis of thin films of manganese (II) 2-ethylhexanoate [6]. The spectra accompanying the photolysis of a film of this complex are shown in Figure 3.

The intermediate is believed to be associated with the breakup of the polymeric structure of the metal 2-ethylhexanoates in the film. The spectral change is presumably the result of a shift as shorted chains are formed. This reflects a larger proportion of the

Figure 2. FTIR spectra of a nickel(II) 2-ethylhexanoate thin film on Si(100) exposed to UV light for 0, 40, 80, 120, 205, 302, 422, 557, 752, and 1412, and 4620 minutes.

Figure 3. FTIR spectra of a manganese(II) 2-ethylhexanoate thin film on Si(100) exposed to UV light for 0, 1, 2, 3, 4, 5, 6, 7, 8, 10, 12, 14, 16, 23, and 38 minutes.

terminal ligands of the chain and the resultant shift in the position of the absorption bands. An analysis of this phenomena has been presented previously [4, 6] and will not be repeated here.

The analysis of the film formed by the photolysis of nickel 2-ethylhexanoate was performed by Auger electron spectroscopy similar to that used for the molybdenum complex except the nickel *LMM* transition was used.

The film was found to consist of nickel contaminated with both carbon and oxygen. Sputtering the surface with argon ions for 45 seconds yielded a surface composed of nickel (65%), oxygen (7%) and carbon (28%).

This result indicated only partial oxidation of the nickel by atmospheric oxygen has occurred. Presumably the bulk of the nickel in this film is nickel (0). Consistent with this interpretation there is still substantial amounts of carbon in the film. Similar results have been observed previously where it was noted that the metal was more prone to retain organic contamination than the metal oxide [12-14].

A similar experiment was done where only half of the film was exposed. This sample was developed with distilled water and the remaining positive pattern subjected to exhaustive exposure. The sample was then

investigated by Auger electron spectroscopy and the result indicated that his sample had the same composition as the sample prepared by the negative process. The results are summarized in Table 1.

Similar Auger electron analysis of the films produced by the photolysis of the manganese(II) 2-ethylhexanoate was done. The material deposited in the negative process was found to be consistent with MnO. The effect of preferential sputtering could affects his result and it should be treated with caution. A similar experiment was done to probe the composition of material deposited in the positive process. In this case after exposure of half the film, the surface was developed with distilled water. The resultant surface was then exposed exhaustively and the surface analyzed by Auger electron spectroscopy. The result indicated the formation of a material of composition indistinguishable from the film formed by negative lithography.

Similar experiments were conducted on films formed by spin coating solutions of barium (II) 2-ethylhexanoate and titanium(IV) di-*n*-butoxide bis(2-ethylhexanoate). The FTIR of the film is shown in Figure 4. Since this represents mixture, a detailed analysis of the spectrum will not be given. The spectrum does appear to be consistent with the presence of bidentate coordinated carboxylate ligands.

The effect of photolysis of the film is loss of all bands associated with coordinated carboxylate ligands and the appearance of a broad band with highest intensity about 1380 cm^{-1} . Similar bands have been seen previously in the deposition of other metal oxides [3, 5]. This band is thought to be associated with the metal oxide film, although it is not possible to rule out that some of the intensity may result from trapped organic material within the film

Figure 4. FTIR spectra of barium(II) 2-ethylhexanoate / titanium(IV) di-*n*-butoxide bis(2-ethylhexanoate) thin film on CaF_2 exposed to UV light for 0, 10, 30 and 60 seconds, 1, 1.5, 2, 3, 4, 5, 6, 8, 10, 13, 17, 22, 28, 35, 45, 65, and 155 minutes.

(see below).

The Auger electron spectroscopy of a surface produced by photolysis then rinsed with hexane was obtained. The composition of the surface of the film indicated barium, titanium and 10% carbon. The surface was cleaned by sputtering which resulted in an increase in the amounts of barium (47%), titanium (7%) and a decrease in the amount of carbon (3%). The results are summarized in Table 2 as the negative process.

A positive process experiment was also conducted on a film formed from barium (II) 2-ethylhexanoate and titanium(IV) di-*n*-butoxide bis(2-ethylhexanoate). In this experiment the sample was exposed through a mask and developed with distilled water. The result, after sputtering, indicates the formation of a deposit consisting of BaO and TiO₂ with some carbon (2%) contamination. The results are summarized in Table 2 under positive (dark area).

Upon examination of the areas of the surface where the film had been exposed, it was evident that some material had been deposited on the surface in this region. This region consisted of barium, titanium, oxygen and carbon. Also evident was the presence of silicon which indicated that the deposit was very thin. The results are summarized in Table 2.

It is worth noting that the original solutions used to prepare these surfaces consisted of a greater ratio of titanium to barium than is observed in any of the analyzed samples. This may be an indication of differential deposition, differential removal or leaching during development. Experiments are currently underway to clarify this issue.

Table 2. Surface analysis of thin films deposited by the photodecomposition of a film formed from barium (II) 2-ethylhexanoate and titanium(IV) di-*n*-butoxide bis(2-ethylhexanoate)

Lithography Method	Sputter Time (sec)	%Ba	%Ti	%O	%C
Negative	0	47.1	5.6	35.8	9.1
	60	47.3	7.2	41.7	3.2
Positive (exposed)	0	33.1	10.0	45.8	9.4
	60**	33.3	11.3	51.9	2.5
Positive (dark area)	0	43.3	7.7	39.8	7.0
	60	47.4	7.4	41.9	2.2

* Cl impurity also observed ** Si observed

3.3. Lithographic Deposition of Metal Oxide

A film of molybdenum (II) 2-ethylhexanoate was exposed through a lithography mask in soft contact with the film. The sample was then developed with hexane. The result is shown in Figure 5A. Clear patterns are evident with micron feature sizes.

Changing the developer from hexane to anhydrous ethanol resulted in the removal of the metal oxide from the film. The result was the positive pattern of the precursor. Exposure of the remaining patterned precursor the led to the result shown in Figure 5B. Energy dispersive spectroscopy confirmed that the deposited material is not the five lines in this image, but rather the surrounding area which is composed of the molybdenum oxide. The features obtainable by this process are comparable to those observed in the negative process.

The composition of the film formed in the positive process was investigated by Auger electron spectroscopy as described previously. The results are summarized in Table 1 and are not significantly different than was observed for the negative process.

Similar results were obtained from conducting contact lithography on films of nickel (II) 2-ethylhexanoate. The lithographic results are shown in Figure 6 and the analysis of the films by Auger electron spectroscopy is presented in Table 1.

Similar results were obtained for manganese (II) 2-ethylhexanoate. Pattern of ca. 3 micron feature size were easily evident in the negative and positive patterns.

Figure 5. SEM images of patterned molybdenum oxide thin films. Images generated by negative (A) and positive (B) lithography.

Figure 6. SEM images of patterned nickel oxide thin films. Images generated by negative (A) and positive (B) lithography.

Figure 7. SEM images of patterned barium titanate thin films. Images generated by negative (A) and positive (B) lithography. (5 kV acceleration voltage)

For the deposited features in all cases were sized in microns and, we believe, the resolution of the features is only limited by the mask used in this study. These are a demonstration of the process rather than a determination of the potential feature size obtainable.

Thin films were constructed by spin coating silicon chips with a solution of barium (II) 2-ethylhexanoate and titanium (IV) di-*n*-butoxide bis(2-ethylhexanoate). The films were exposed through an optical mask in contact mode. Development with hexanes yielded the negative image shown in Figure 7A.

A change in the developing solvent to distilled water results in the formation of a positive image. Development was followed by exhaustive exposure and led to the image shown in Figure 7B. Features of similar size to those achievable in the negative image were obtained.

It is interesting to note that positive lithography of the barium-titanium oxide film is rendered possible by the presence of both

precursors. We have been unable to perform positive lithography when either precursor is used alone. It is only when the two precursors are combined that we have been able to demonstrate the development of the latent image, leading to successful positive lithography.

4. Discussion

Lithography relies on the different solubilities between the exposed and unexposed regions. In all the cases presented in this paper, negative lithography is carried out by extensively converting the precursor to the metal oxide (Scheme 2, Steps A-C) in the exposed regions. The metal oxide is typically insoluble in organic solvents, while the precursor remaining in unexposed areas remains soluble and can be developed (Scheme 2, Step D).

For example, both the manganese (II) and molybdenum (II) 2-ethylhexanoates were developed using the same solvent used to spin coat the precursor film. In these cases, unconverted (unexposed area) metal(II) 2-ethylhexanoate remains soluble in hexane, while the metal oxide (exposed area) is insoluble in hexane. This results in negative patterning, as can be seen in Figures 5A, 6A and 7A.

To carry out positive photolithography, the precursor thin film is exposed to a small dose of UV light, insufficient to fully convert the precursor thin film to the metal oxide, but sufficient to partially convert the precursor film to the metal oxide, an intermediate or both. In any case the exposed region now consists of a mixture (Scheme 2, Steps A and E). This mixture can then, at least in theory, be developed, since it has a different solubility than the unconverted precursor film. The result is a positive image in the precursor thin film (Scheme 2, Step F). Upon blanket exposure to UV light, this image can then be fully converted to the metal oxide (Scheme 2, Step G, and Figures 5B, 6B, and 7B), as in the negative photolithography.

We suggest three possible mechanisms by which the solubility of the intermediate is changed enough to allow positive image developing.

a. Polymeric fragmentation. As was discussed in Section 3.1 and references [4-6], upon exposure to UV light, the coordination of metal centers via bridging carboxylate

Scheme 2. Photoresist free, negative (Steps A-D) and positive (Steps A & E-G) photolithography of metal oxides from metal 2-ethylhexanoates. See text for description.

groups is fragmented. It is well known that oligomeric or monomeric species tend to have a higher solubility than polymeric species. Hence, partial defragmentation of the polymeric network by light may yield differential solubilities, and allow the positive image to be developed.

b. Mixture Formation. As was pointed out above, the exposed region is converted into a mixture of precursor metal oxide and potentially an intermediate. This mixture has and inherently different solubility than the precursor film. The presence of metal oxide in this precursor should render it more hydrophilic. This is consistent with the effectiveness of more polar solvent in developing the positive patterns.

c. Metal oxide nucleation sites. As the precursor thin film undergoes conversion to the metal oxide, it is possible that metal oxide growth occurs around nucleation sites. As the photochemical reaction is carried on, the number of nucleation sites increases. Thin films containing metal oxide clusters in unconverted precursor may have less cohesion than either unconverted or fully converted thin films. As such, this weaker cohesion could allow the development of the positive image.

Most likely, all three of the above

mechanisms play a role at some point during the photochemical reaction, and the overall effect enhances the potential of this family of precursors to undergo positive photolithography.

5. Conclusion

We have demonstrated that metal(II) 2-ethylhexanoate metalorganic compounds are suitable precursors for the direct, photoresist free photolithographic deposition of metal oxide. These precursors can be used to lithographically deposit both the positive and the negative images of the amorphous metal oxide. We have demonstrated that micron scale feature size structures are readily obtainable by both positive and negative lithography from metal organic complexes.

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