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Photolithographic Olefin Metathesis Polymerization

Raymond A. Weitekamp,[†,‡] Harry A. Atwater,[‡] and Robert H. Grubbs*[,†]

[†]Arnold and Mabel Beckman Laboratories for Chemical Synthesis, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, United States

[‡]Thomas J. Watson Laboratories of Applied Physics, Division of Engineering and Applied Science, California Institute of Technology, Pasadena, California 91125, United States

S Supporting Information

ABSTRACT: Patterning functional materials is a central challenge across many fields of science. The ability to lithographically fabricate micro- and nanostructures has been one of the most impactful technological breakthroughs of the last century. In part due to the complexity of the chemical processes in photoresists, there is a limited variety of materials that can currently be patterned by photolithography. We report a negative tone photoresist using a photoactivated olefin metathesis catalyst, which can be quickly prepared in a one-pot synthesis from commercially available starting materials. The resist is based on a ruthenium vinyl ether complex, widely regarded as inactive toward olefin metathesis. The combination of this photoactivated catalyst with the fidelity and functional group tolerance of ruthenium-mediated olefin metathesis enables a host of new possibilities for photopatterned materials.

Photolithography is the patterning technique at the foundation of microfabrication, the core of modern integrated circuit technology. In a photoresist, the pattern of optical irradiation is converted to a pattern of chemically distinct regions, typically through photoinitiated functional group cleavage or cross-linking. Many modern photoresists employ the concept of "chemical amplification", in which a photogenerated catalyst reacts with many sites.[1,2] For example, photoacid generators are commonly employed in chemically amplified resists, either to catalyze a ring-opening polymerization or initiate a cascade of deprotective bond scissions within a polymer matrix, imparting new solubility properties to the irradiated regions. While there are a number of light-mediated reactions that could in principle be employed in photolithography, very few have been implemented. Despite the fact that there are hundreds of commercially available photoresists, the functional diversity among these materials is severely limited. In most applications, the photoresist serves the sole purpose of a sacrificial mask or mold; very rarely is the resist material incorporated as a structural element or chemically functional interface. The ability to generate new kinds of chemically functional materials directly via photolithography would enable a host of new applications, for example, in microelectromechanical systems (MEMS), microfluidics, patterned biomaterials and artificial optical materials.

Olefin metathesis is a robust synthetic methodology that has led to new polymeric materials with many applications, such as drug delivery,[3] organic electronics,[4] and photonic crystals.[5,6] A number of latent olefin metathesis catalysts have been developed, using variety of activating stimuli, including pH, heat and light.[7,8] Photoinitiated ring-opening metathesis polymerization (ROMP) has been demonstrated with many different transition metals, including tungsten,[9] ruthenium,[10−12] and molybdenum.[13] Photoinitiation mechanisms include triggered alkylidene formation,[9] as well as ligand dissociation through both direct photoexcitation[10] and indirectly via a photoacid generator.[11,12] Despite these many examples, an olefin metathesis based photoresist has not yet been developed. Part of the challenge in developing such a system is achieving a stark contrast between the reactivity of the catalyst in the light and the dark. Additionally, the requirements of ambient stability and processability present barriers to the industrial implementation of transition metal based photocatalysts. In this communication, we demonstrate that the standard quenching procedure for ROMP reactions generates a photoactive latent catalyst and exploit this serendipitous discovery in the facile synthesis of a new family of photocurable materials.

The addition of vinyl ethers is a widely employed method of quenching ROMP reactions.[14] The regioselective formation of vinyl ether complexes is extremely rapid and irreversible under certain conditions, leading to the use of vinyl ether "trapping" as a tool for determining catalyst initiation rates.[15] The resultant Ru "Fischer-type" carbenes are generally considered to be unreactive, although our group previously reported that some of these complexes can be competent olefin metathesis catalysts at elevated temperatures.[16] Quenching a living ROMP reaction yields a methylene-terminated polymer chain and a presumably 14-electron ruthenium vinyl ether. While the phosphine or pyridine ligands typically found on ruthenium ROMP catalysts could in principle recoordinate to the quenched complex, the statistical likelihood of this is low considering the concentration and stoichiometry of typical ROMP reactions. In addition, the air-sensitivity of the ruthenium vinyl ether complexes certainly aids in the quenching process, through almost immediate decomposition of the alkylidene species. A typical quenching procedure utilizes excess vinyl ether and immediate precipitation of the polymer to remove the catalyst. We show that if this sensitive ruthenium vinyl ether complex can be stabilized, reactivity can be retriggered by ultraviolet (UV) irradiation.

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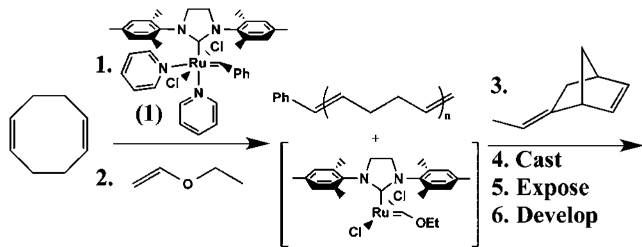
Here we report a method of patterning using a ruthenium photocatalyst, which we term PhotoLithographic Olefin Metathesis Polymerization (PLOMP). In this procedure, a latent metathesis catalyst is activated by light to react with the olefins in the surrounding environment. We demonstrate a negative tone resist by using the photocatalyst to cross-link a difunctional ROMP monomer within a matrix of linear polymer. In principle, a positive tone resist could also be developed, by using light-triggered secondary metathesis events to increase the solubility of the irradiated regions. This can be considered a "chemically amplified" resist, in that the photoactive species is a catalyst for the cross-linking of the polymer matrix. The versatility of ruthenium-mediated olefin metathesis can now be utilized to photopattern a variety of functional materials via PLOMP, advancing the field of photoinitiated olefin metathesis from a curiosity to materials science applicable to mass microfabrication.

Our one-pot preparation from commercially available starting materials can be completed in the span of a few hours. It should be noted that the photoactive vinyl ether complex is sensitive to oxygen, heat and light. Preparation of the resist should be carried out under an inert atmosphere for best results. First, complex **1** is employed to afford the ROMP of 1,5-cyclooctadiene (COD) (Scheme 1). This reaction is sufficiently

Scheme 1. The One-Pot Preparation of a PLOMP Resist



complete in minutes and subsequently quenched with ethyl vinyl ether. After removing the volatiles in vacuo, the linear poly(COD) is dissolved in a difunctional monomer, such as 5-ethylidene-2-norbornene (ENBE). The chemical composition and molecular weight of the linear polymer, the amount of ENBE and the excess of vinyl ether can all be modulated to tune the properties of the photoresist. The presence of some excess vinyl ether is beneficial for mitigating dark polymerization of the resist material. In our PLOMP resists, the high viscosity of the solution as well as the possibility of dative bonding from the surrounding olefins likely contribute to stabilizing the photocatalyst (Figure 1). Despite the sensitivity of the ruthenium vinyl ether complexes, we found that viscous resist solutions could be used successfully under ambient benchtop conditions for many weeks.

These olefin rich solutions proved to be competent UV photoresists, at both 254 and 352 nm. Silicon coupons (1 cm^2) were cleaned with piranha and rinsed with copious amounts of deionized water, isopropyl alcohol, and acetone. For consistent adhesion, the coupons were first heated to 150 °C for 1−2 min to remove adventitious moisture and cooled under a stream of argon immediately prior to casting. Approximately 0.1 mL of the resist solution was deposited on each 1 cm^2 coupon and spun at 2500−7000 rpm for 60 s, depending on the desired thickness. Under 254 nm irradiation, we were able to cure 1−2 μm thick films in 60 to 90 s using a benchtop 8-W lamp. With our 352 nm blacklight bulb, the necessary exposure times were

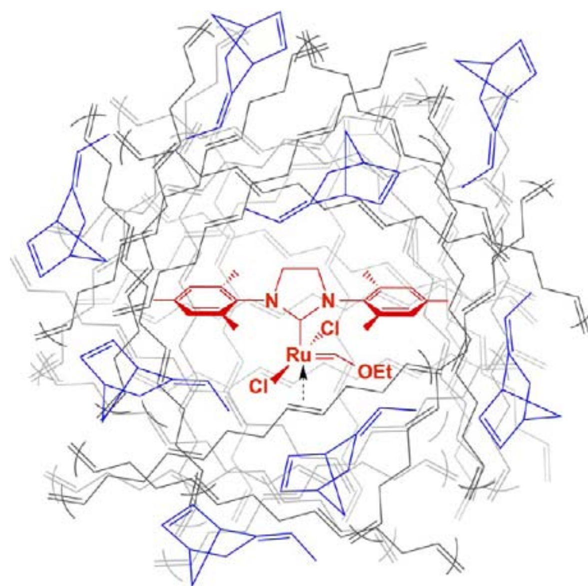


Figure 1. A cartoon depicting the proposed environment of the PLOMP resist. We propose that the viscous, olefin rich solution stabilizes the sensitive vinyl ether complex through dative bonding, as depicted. The photoactivated catalyst (red) cross-links the ethylidene norbornene molecules (blue) into the matrix of poly(COD) (gray).

significantly longer, ranging from 5 to 15 min depending on the batch and film thickness. Films up to approximately 500 nm thick were patterned at wafer scale using printed photomasks (Figures 2 and 3). We were able to reliably fabricate bar

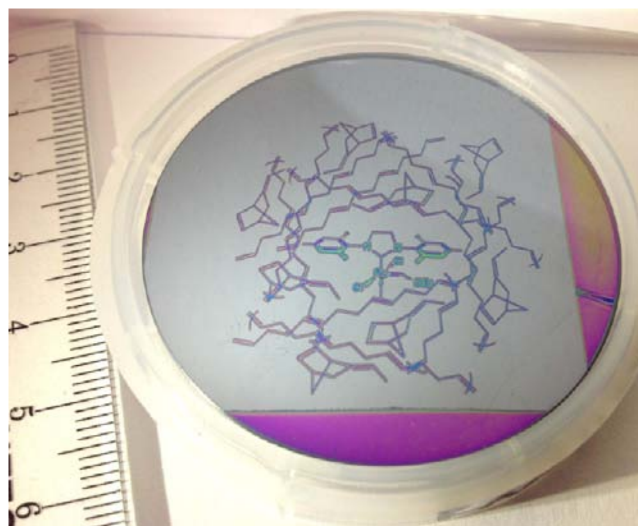


Figure 2. PLOMP was used to pattern a 2 in. diameter silicon wafer with a blacklight lamp (λ = 352 nm) and a printed photomask.

structures with a width and spacing down to 30 μm with good fidelity (Figure 2). Optimization using a commercial mask aligner and collimated source will certainly improve the resolution and fidelity of our PLOMP resists. While we were able to work with some batches of the resist under ambient conditions for many weeks before the performance deteriorated, a significant delay between spin-casting and exposure led to inconsistent results. This is not surprising, considering the increased surface-to-volume ratio after spin-casting and the known air-sensitivity of these vinyl ether complexes. The onset

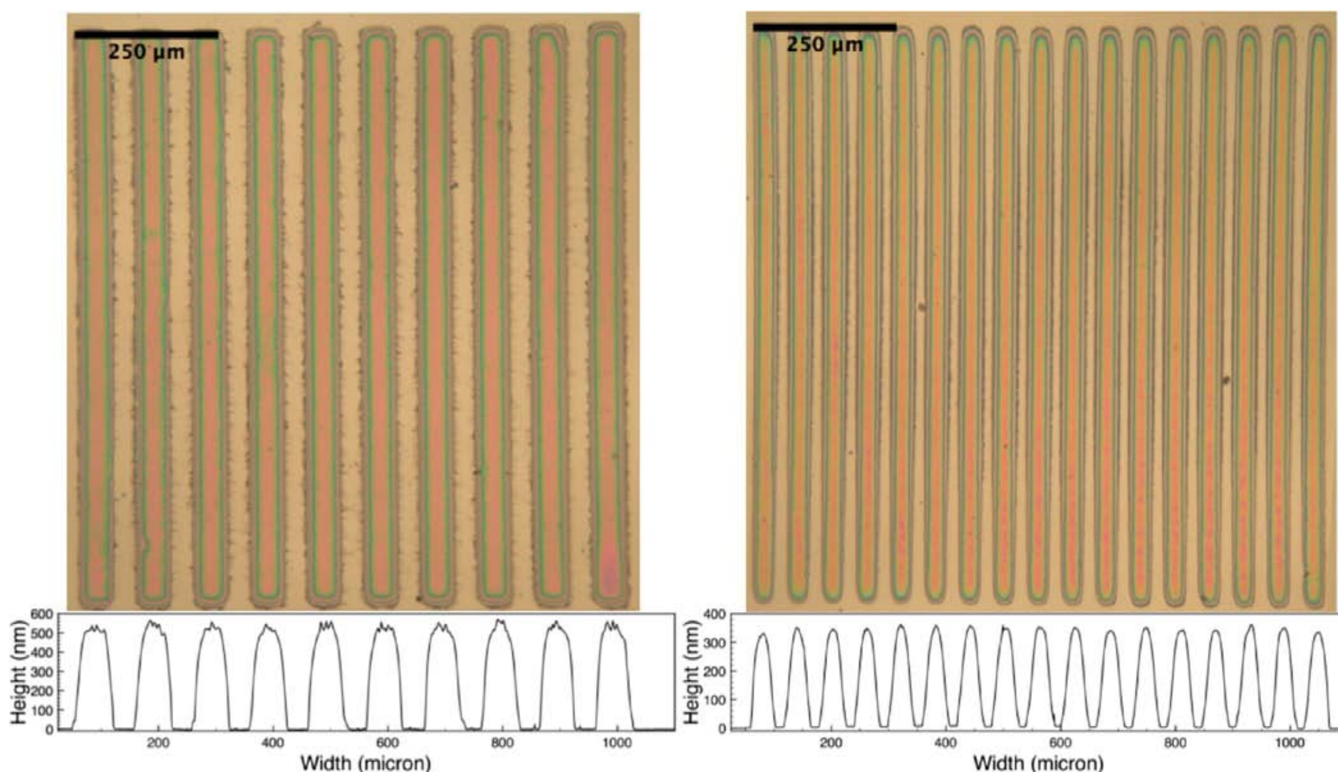


Figure 3. (Top) Micrographs of 1 mm long bars, with widths of 50 μm (left) and 30 μm (right). (Bottom) The height profiles of the same bar arrays are shown, as measured by profilometry.

of background (dark) cross-linking of the difunctional monomer may also contribute to this observation.

One advantage of our PLOMP resist over many commercial resists is the ability to maintain surface adhesion to the native oxide surfaces of silicon wafers without any etching or surface derivatization. By contrast, many commercial photoresists require HF etching of the oxide and/or surface derivatization with reactive molecules such as hexamethyldisilazane. In this respect, our PLOMP resists offer a safer and more versatile alternative, as the polymer composition can be easily tuned to modulate adhesion. Additionally, PLOMP resists do not require postexposure baking to develop. Currently, ruthenium-mediated ROMP is employed in a number of industrial scale applications, including high-modulus resins and extremely chemically resistant materials. PLOMP can provide UV-curable and patternable coatings with these desired materials properties. Finally, the ability to generate many batches of resist in a single workday enables rapid prototyping for future development.

We have demonstrated a novel photoresist based on olefin metathesis. The detailed mechanism of photoactivation remains uncertain and is an ongoing research focus. Functional diversity can be incorporated into PLOMP resists in a number of ways, including copolymerization of COD with another monomer and incorporation of additives into the resist solution, as well as postpolymerization modification of the olefin-rich cross-linked material. We have successfully incorporated a variety of functional groups into the resist material, including esters, acids, ethers, and isocyanates. We anticipate that PLOMP will enable the development of directly patterned micro- and nanostructures with chemical, mechanical, and optical functionality not currently available with existing fabrication techniques.

■ ASSOCIATED CONTENT

Supporting Information

Materials and methods, supplementary experiments, Figures S1−S3. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

rhg@caltech.edu

Notes

The authors declare no competing financial interest.

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