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Photolithographic Patterning of Ring-Opening Metathesis Catalysts on Silicon**

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The patterning of polymers on surfaces for use in applications such as organic electronic systems,[1] optical devices,[2] photoresist technology,[3,4] and biological sensors[5] has attracted increasing attention in recent years. Surface-bound polymers can be created by a variety of methods, including radical, anionic, and cationic polymerization,[6–9] scanned-probe lithography,[10] inkjet[11] and screen printing,[12] spin-coating,[13] and self-assembled monolayer formation via micro-contact printing (μCP).[14–16] In addition, it has been demonstrated[4,17–19] that patterned, surface-bound polymers can be grown on surfaces using μCP in conjunction with ring-opening metathesis polymerization (ROMP). One limitation of the current methodologies for the patterning of surface-bound polymers is the lack of compatibility with conventional photolithographic technologies. A photolithographic ROMP-based method for creating patterned polymers would facilitate the creation of non-silicon-based structures using protocols that are consistent with those employed in the fabrication of silicon-based structures. In this report, we demonstrate the photolithographic patterning of ROMP catalysts on oxide layers above Si(100) surfaces and the subsequent growth of both linear and highly crosslinked polymers on these surfaces.

Recent reports have provided insights into the thermolytic decomposition pathways of typical ruthenium carbene complexes used in olefin metathesis[20] and have elucidated the mechanism and activity of this class of catalyst.[21] This work pointed to the dissociation of a phosphine ligand as a critical step in both the activity of the catalyst and its lifetime. It has also been demonstrated[22] that exposure of the ruthenium catalyst **2** to UV light causes a photochemical release of the phosphine ligand. The release of the ligand in the presence of a suitable monomer results in an increase of catalyst activity. We hypothesized that if photo-induced phosphine release was carried out in the absence of a monomer, side reactions could render the catalyst inactive. We verified this hypothesis by dissolving catalyst **2** in methylene chloride, exposing the solution to UV light for varying time intervals, and then introducing norbornene monomer. The degree of polymerization decreased with increased exposure time, and with sufficient exposure time polymerization could be eliminated completely. We also found that if the inactivation process was performed under an inert atmosphere, the catalyst remained competent even after prolonged exposure to UV light. While the exact mechanism of light-initiated catalyst decomposition is unknown, ^{1}H NMR analysis of post-exposure catalyst solutions indicates the presence of benzaldehyde. It is unlikely that photodeactivation of the catalysts proceeds via the same bimolecular mechanism[20,21] observed for deactivation in the absence of irradiation, particularly on surfaces. Ongoing studies should provide more insight into the exact mechanism of inactivation.

Having demonstrated the photodeactivation of ROMP catalysts, we sought to use this technique to pattern polymers on surfaces via the scheme in Figure 1a. Si(100) wafers (1 cm × 1 cm) with a 10 000 Å oxide layer were functionalized with trichloro(5-norbornen-2-yl)silane **1** and then exposed to a ruthenium metathesis catalyst in order to bind the catalyst to the surface. Catalyst inactivation was effected by exposing the entire surface of the wafer to UV light for 45 min. The wafers were then placed in a solution of norbornene **6**. As expected, there was no appreciable polymer growth on exposed wafers when compared to unexposed control wafers. This methodology proved successful with all surface-bound variants of Grubbs' ruthenium-based metathesis catalysts that we investigated: **2**, $\mathrm{RuCl_2(PCy_3)_2({=}CHPh)}$,[23] **3**, $\mathrm{RuCl_2(H_2IMES)(PCy_3)}$ $\mathrm{({=}CHPh)}$,[24] **4**, $\mathrm{RuCl_2(H_2IMES)\ (Py)_2({=}CHPh)}$,[25] and **5**, $\mathrm{RuCl_2(H_2IMES)}$ $(m\text{-}\mathrm{BrPy})_2\mathrm{({=}CHPh)}$(**5**)[26] (Fig. 1b).

Having established that surface-immobilized ruthenium metathesis catalysts can be inactivated using light, the possibility of selective inactivation using a simple photolithographic technique was investigated. A wafer with ruthenium catalyst bound to the surface was placed in direct contact with an optical test mask (Fig. 2a). The mask and wafer were then

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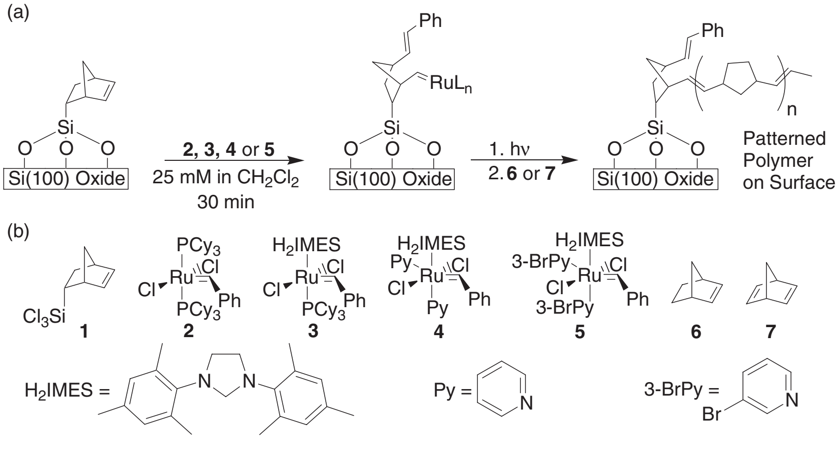

Figure 1. a) Procedure for functionalization of silicon oxide surfaces and for photopatterning polymers on them. b) Silane, catalysts, and monomers used in this methodology.

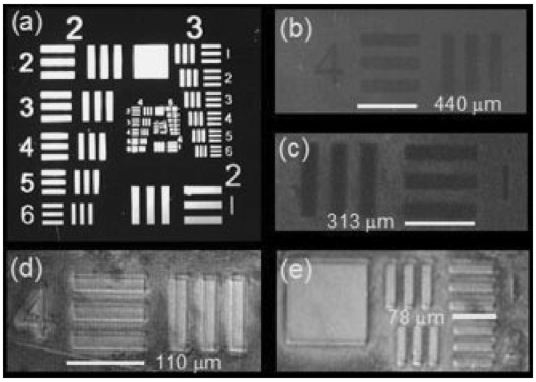

Figure 2. a) Optical micrograph of the United States Air Force (USAF) test mask used in the creation of patterned polynorbornene on Si(100) oxide layers. b) Polynorbornene patterned on a silicon wafer using catalyst **2**. c) Optical image of patterned polynorbornene created with catalyst **3**. d) Optical image of patterned polynorbornene created with catalyst **4**. e) Optical image of patterned polynorbornene created with catalyst **5**.

exposed to UV light from a fiber-optic UV light source. After exposure, the wafer was placed in a 1 M solution of norbornene in CH$_2$Cl$_2$. After 5 min, patterned polymer features were visible to the naked eye.

The results of typical patterning experiments using different catalysts are shown in Figure 2b–e. It is apparent from these results that it is possible to achieve features that are 78 μm long and approximately 20 μm wide (Fig. 2e). It is also clear from these images that there is a correlation between the quality of the pattern and the activity of the ROMP catalyst. The more active catalysts, **4** and **5**, generate patterns with higher resolution and thicker, more uniform polymer layers. In trials with catalysts **4** and **5**, clean lines with lengths of 21 μm and widths of 4.3 μm could be fabricated. Scanning electron microscopy (SEM) indicated that the edge roughness of the features is less than 1 μm. By varying reaction conditions such as monomer concentration or polymerization time, polynorbornene film thicknesses ranging from 500 to 50 000 Å could be created, as determined by profilometry. In addition, the immobilization of catalysts **4** and **5** on the surfaces affords the opportunity to explore employing less reactive monomers in this methodology. For example, monomers such as norbornadiene (**7**), which possesses a second double bond, can be crosslinked after ROMP polymerization, resulting in a stronger, etch-resistant polymer that could have uses in polymer-based micromechanical electrical systems (MEMS).

To determine the feasibility of using norbornadiene in this methodology, catalyst **5** was immobilized on a 10 000 Å oxide layer on Si(100) and patterned as described above. The wafer was then immersed in neat norbornadiene for 60 min. This extended growth time was necessary due to norbornadiene's lower reactivity in ROMP. The resultant polynorbornadiene films are thinner (500 to 3000 Å) than those created with norbornene, but the differences between the exposed and unexposed regions of the wafer are still readily apparent (Fig. 3a). The regions lacking polymer growth retain the wafer's original pink color, while the regions where the polymer has grown exhibit a bluish-green color. The surface-bound polymer was crosslinked by dipping the patterned wafer in neat di-*tert*-butyl peroxide[27] and gently heating at 50 °C. After the crosslinking, the wafer was etched for 15 mins in a buffered HF solution. After etching, the patterned polynorbornadiene film is clearly visible and the regions that lack polymer growth change in color from pink to the blue of bare silicon (Fig. 3b). Polynorbornadiene films grown in this man-

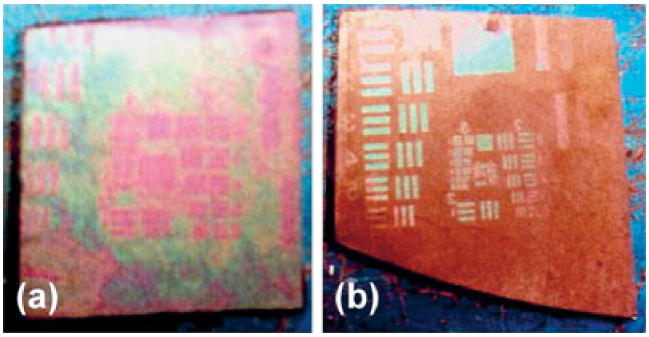

Figure 3. a) An optical micrograph of patterned polynorbornadiene grown on a Si(100) thermal oxide layer. The pink areas are the regions with no polymer growth. The wafer is approximately 3 cm × 3 cm. b) A Si(100) wafer that was etched after patterned polynorbornadiene was grown on the surface oxide layer. This wafer is also approximately 3 cm × 3 cm. The change in color of the unprotected regions on the wafer indicates that etching was successful.

ner that were not subjected to the crosslinking procedure underetched in 15 min and detached from the surface. These experiments demonstrate the feasibility of using unsaturated monomers to grow patterned crosslinked polymers on silicon surfaces using ROMP.

In conclusion, we have demonstrated an approach that affords covalently attached patterned polymers on silicon wafers in a manner that is compatible with conventional lithographic techniques. Although the results reported here involve patterning on a silicon oxide layer, the technique is equally applicable to patterning using ROMP catalysts that have been bound directly to silicon using the chemistry of Juang et al.[17] Our methodology is compatible with a range of ruthenium-based olefin metathesis catalysts and monomers, providing great flexibility for the creation of polymers with different desirable properties, including mechanical strength and etch resistance. The technique reported here may find use in a range of hybrid technologies in which polymers are patterned on silicon, including organic electronic devices and polymer MEMS.

Experimental

Si wafers (3″, oxide layer 10 000 Å, resistivity 1–10 Ω cm, p-type, boron dopant, orientation (100), one-side polished, purchased from University Wafer.) were cleaned with a 3:1 H_2SO_4/H_2O_2 solution for 1 h, rinsed with 18 MΩ water, dried under a stream of N_2, and stored in a dessicator prior to use. Unless otherwise noted all reactions were carried out in flame-dried glassware using distilled solvents. Trichloro(5-norbornen-2-yl)silane **1** was synthesized based on a published procedure [28]. Ruthenium catalysts **4** [25] and **5** [26] were synthesized via published procedures. Ruthenium catalysts **2** and **3** were purchased from Strem or Aldrich and used as received. Norbornene, pyridine, 3-bromopyridine and di-*tert*-butyl peroxide were purchased from Aldrich and used as received. Norbornadiene was purchased from Aldrich and was purified by passing through an aluminum oxide column prior to use. The UV deactivation of catalyst was carried out with a Hamamatsu Lightning Cure 200 series lamp (model number: L7212-01; lamp type: mercury-xenon; output intensity: 3500 mW cm^{-2}). Surface oxide etching was achieved using a 6:1 NH_4F (40 % aq.)/HF solution.

*Functionalization of Silicon Wafers with Trichloro(5-norbornen-2-yl)silane **1***: A 4 dram screw-cap vial (Fisher cat #03-339-21 J) was charged with 1 mL of a solution of trichloro(5-norbornen-2-yl)silane (0.100 mL) in distilled toluene (10 mL). A 1 cm × 1 cm piece of silicon wafer with a thermal or native oxide layer was added to the solution. The solution was agitated on an orbital shaker at room temperature for 12 h. The silane solution was decanted and toluene (2 mL) was added. The wafers were shaken for 5 min and then the toluene was poured away. A second aliquot of toluene (2 mL) was added and the wafer was sonicated for 1 min. The wafers were then dried under a dry nitrogen stream. The wafers were stored in a dessicator prior to use.

Immobilization of Ruthenium-Based Metathesis Catalysts to Silicon Wafers Functionalized with Trichloro(5-norbornen-2-yl)silane: A silane-functionalized wafer was placed in a 4 dram screw-cap vial. 2 mL of a 25 mM solution of catalyst **2**, **3**, **4** or **5** in CH_2Cl_2 was added to the vial. The solution was shaken for 30 min. The solution was removed and CH_2Cl_2 (5 mL) was added. The wafers were shaken for 5 min and the solvent was decanted. The process was repeated until the CH_2Cl_2 washings were no longer colored (usually 3 washings). The wafers were used directly in pattering studies after functionalization.

Patterning of a Catalyst-Functionalized Wafer with Ultraviolet Light: A wafer loaded with active catalyst was attached to an optical mask containing the desired pattern. The optical mask was then placed in direct contact with the light source. The wafer was exposed to the light through the mask for 45 min. After exposure, the wafer was immediately used in the subsequent polymerization step.

General Procedure for the Growth of Polynorbornene Films on a Surface: A patterned wafer was immersed in a 1 M solution of norbornene in CH_2Cl_2 for 5 min. The wafer was removed, rinsed with CH_2Cl_2 and dried under a stream of dry N_2.

General Procedure for Growing Polynornadiene Films on a Surface: A patterned wafer was immersed in neat norbornadiene for 60 min. The wafer was rinsed and then dipped in neat di-*tert*-butyl peroxide. The wafer was gently heated at 50 °C for 2 min. This process was repeated 3 times. After the peroxide treatment, the wafer was etched using buffered HF.

Profilometry: A razor blade was used to cut through the polymer film perpendicular to the polymer/silicon interface. The depth of the film was measured across this cut with a profilometer (Tencor Alpha-Step 500 Surface Profiler). A scan length of 0.1 mm or 0.2 mm was used with a tip speed of 0.002 mm per second. The vertical range/resolution of the measurements was 13 μm/1 Å or 300 μm/25 Å, The sampling rate for all the measurements was 50 Hz. The profile type for all the scans was “center bias”. All of the measurements were performed using the continuous scan mode.

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Three-Dimensionally Oriented Aggregation of a Few Hundred Nanoparticles into Monocrystalline Architectures[**]

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Surface-stabilized nanoparticles, acting as nanoscale building blocks, can spontaneously self-assemble into various ordered nanostructures, a process which is usually controlled by altering the surface properties of particles using organic-coating layers.[1–5] It has been well established that organic ligands with high nanoparticle binding affinities can promote self-assembly, driven by the interactions between surface-adsorbed ligands instead of between the particles themselves. In the absence of sufficiently strong surface-protecting layers, it seemed that nanoparticles would always randomly aggregate into disordered solids. However, recent demonstrations of self-organized aggregation of such nanoparticles to yield ordered-crystal structures came as a surprise.[6–10] Ordered self-assembly requires that aggregated nanoparticles can equilibrate with non-aggregated ones in solution and adjust their positions relative to one another in an aggregate. The aggregation-driven growth of nanoparticles into single-crystalline architectures is usually realized upon the controlled removal of appropriate organic additives at interfaces and the subsequent oriented attachment of nanoparticles by rotating adjacent nanoparticles so that they share an identical crystallographic orientation.[8,11] The normal concept for crystal growth, which is typically thought to occur via atom-by-atom addition to an existing nucleus or template, has been challenged by the aggregation-based growth of nanoparticles. A few examples of aggregation-based growth have been reported recently, such as the fusion growth of Ag nanoparticles into nanoprisms,[12] the ligand-directed assembly of preformed titania nanocrystals into highly anisotropic nanostructures,[13] and the spontaneous aggregation of iron oxyhydroxide into larger defective monocrystals in iron-oxidizing bacteria.[6] In addition, oriented aggregation of nanoparticles has also led to the formation of other low-dimensional crystalline materials such as ZnO nanorods,[7] CdTe nanowires,[8] and α-Fe$_2$O$_3$ disks/ellipsoids.[14,15]

Since the oriented-aggregation growth of a limited number of nanoparticles into low-dimensional crystalline nanomaterials has been demonstrated through linearly oriented attachment, it is our goal to observe and understand the three-dimensional (3D) orientation and aggregation process of a few hundred nanoparticles into a single-crystalline 3D structure. Here we report a simple synthetic approach to building monocrystalline CuO from nanoparticles at room temperature. We have demonstrated an anisotropic aggregation-based crystal-growth process of a few hundred monoclinic CuO nanoparticles into uniform ellipsoidal monocrystalline architectures. Stepwise orientation and aggregation of a large number of nanoparticles in three dimensions has been observed, from the formation of primary CuO nanoparticles, to the preferential one-dimensional (1D) orientation of nanoparticles along the (001) direction at an early stage, and, eventually, 3D-oriented aggregation into a monocrystalline structure built from nanoparticles. Selective adsorption of formamide molecules on different crystallographic planes of monoclinic CuO nanoparticles may play an important role in the anisotropic growth of uniform nanoparticle-built monocrystals. The understanding of the oriented-attachment mechanism may further open up new opportunities to fabricate complex low-dimensional or 3D nanostructured materials and provide new insight into the aggregated biomineralization mechanism of nanoparticles.

Copper oxide has been of considerable interest because it forms the basis of technologically important materials such as high-temperature superconductors and plays practical roles in catalysis, sensing, and solar-energy transformation.[16–20] The ability to fabricate nanostructured copper oxide has further prompted a renewed interest in enriching our understanding of its fundamental properties and enhancing its performance in currently existing applications. Copper oxide nanoparticles have recently been prepared by a number of methods, including thermal decomposition, oxidation, reduction, and hydrolysis of metal or metal salts.[16–21] In the research reported here, aggregation-based formation of nanostructured copper oxide particles has been achieved through a simple natural oxidation of copper metal in formamide and subsequent hydrolysis of the resulting copper–formamide complexes in aqueous solution, as detailed in the Experimental section. The powder X-ray diffraction (XRD) pattern of the as-synthesized sample in Figure 1A confirms the formation of crystalline monoclinic CuO (cupric oxide) (Joint Committee on Powder Diffraction Standards file No. 74-1021). Uniform ellipsoidal particles of cupric oxide were revealed by low-magnification transmission

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