Secondary Patterning of UV Imprint Features by Photolithography

Martha F. Montague[†,‡] and Craig J. Hawker*[,‡,#]

Center for Nanotechnology and Department of Chemical and Biological Engineering, University of Wisconsin, Madison, Wisconsin 53706, IBM Almaden Research Center, San Jose, California 95120, and Materials Research Laboratory, Departments of Chemistry and Materials, University of California, Santa Barbara, California 93106

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An acid-cleavable cross-linker (2,5-dimethyl-2,5-hexanediol dimethacrylate or DHDMA) was prepared and patterned with UV imprint lithography (UV-IL) to create cross-linked films that could be secondarily patterned in a subsequent photolithographic step. The thermal and acid-catalyzed decomposition of DHDMA films were measured with both attenuated total reflectance FTIR and ellipsometry, which showed that images could be formed in cross-linked films by exposure to 254 nm radiation in the presence of a polystyrene overcoat containing a photoacid generator (PAG). As a resist for imprint lithography, DHDMA could be patterned with feature sizes ranging from tens of micrometers to 120 nm, and in films with thicknesses from 2 μm to 500 nm, whereas the second photolithographic step allowed the subsequent micrometer-sized patterning of these original features. The modular nature of this novel two-step patterning process allows the imprinting of DHDMA with functional comonomers such as *p*-acetoxystyrene, demonstrating the extension of this concept to additional chemistries and further tailoring of resist performance.

Introduction

As nanopatterning technologies have advanced and become more accessible, patterned substrates are finding application in an increasingly wide range of fields. In addition to the microelectronics industry, nanopatterned substrates are now being developed for biocompatible surfaces,[1,2] microanalytical devices,[3,4] and organic electronics.[5,6] However, these new applications have very different materials requirements compared to the microelectronics industry, which creates a demand for modified patterning techniques that are compatible with a wider range of materials. One example of this is in the development of biocompatible surfaces, which are created to mimic the complex chemical and topographical structures that are present in biological substrates.[7] Although recent research has demonstrated the effects of substrate chemistry[8] and topography[9] on cell behavior, in order to create surfaces that capture all of the detail of biological surfaces, techniques are needed that allow for patterning of a range of chemistries as well as structures. Additional examples of applications for patterning new materials include nanofluidics for microanalytical systems, in which optimization of surface chemistry can minimize absorption of analytes,[10] and in the developing area of organic electronics, which is based on plastic substrates that are not compatible with many of the traditional microelectronic patterning techniques and processing conditions.[5,6]

Historically, nanopatterned structures have been created with optical lithography, in which photoinduced reactions create solubility changes in a polymeric thin film that lead to pattern formation[11] or via self-assembling systems.[12] One of the limitations of this technique is that the process of image formation is dependent on resist chemistry, which makes simultaneous tailoring for other applications difficult. In contrast, the emerging field of imprint lithography allows for the separation of chemistry from image formation,[13−15] which dramatically increases the range of patternable materials. The simplicity of imprint lithography also allows nanopatterning techniques to become accessible to nonexperts, thereby expanding the impact of the field and further fueling the demand for new materials.

Imprint lithography falls into two main categories, thermal imprint lithography (T-IL)[16] and UV imprint lithography (UV-IL),[17−19] each of which is used with a different set of

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* Corresponding author. E-mail: hawker@mrl.ucsb.edu.
[†] University of Wisconsin.
[‡] IBM Almaden Research Center.
[#] University of California, Santa Barbara.

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resist materials. Specifically, T-IL is used to mold films using heat, typically thermoplastic polymers such as PMMA, whereas UV-IL starts with a low-viscosity mixture of cross-linkers and a photoinitiator and exposure to UV radiation cross-links the resist. Of the two systems, UV-IL has the greatest potential for new applications because the printed films are cross-linked and therefore stable to a variety of postprocessing applications. Additionally, because the UV-IL systems do not require a heating step and typically operate at lower pressures, they have faster cycle times as well as a greater diversity in selection of functional groups.[20]

Since the first demonstration of nanoscale imprinting, UV-IL has been used to create a number of devices, including field-effect transistors[21,22] and patterned magnetic media.[17] To fully explore the potential of this system and increase its versatility, it is highly desirable to develop new resist materials that have added functionality. One area of resist design that would benefit from increased functionality is in the nature of the cross-linker for UV-IL imprinted films. Typically, this in an unfunctionalized cross-linker such as trimethyloyl triacrylate, which is difficult to degrade, and consequently, imprint systems based on such systems have limitations associated with their use. By designing a resist in which all of the cross-linkers are cleavable under mild acid conditions, we would require only a simple degradation step to remove the film after imprinting. Not only does this allow for the selective removal of the imprinted film in the presence of other organic/biological materials (which would be damaged during a traditional etch step) this also creates a secondary mechanism for patterning exploiting traditional photolithography. To demonstrate the use of functionalized cross-linkers in imprint lithographic, we report the combination of imprint and optical lithography into a single system by employing acid-cleavable cross-links into the original imprint lithographic system. By carefully tailoring the sensitivity of the acid-cleavable cross-linkers, the possibility also exists to secondarily pattern the imprinted films by exposure to light in the presence of photoacid generators.[12,23] In addition, such a two-step strategy allows for the creation of a wider range of features than each technique could create individually. For example, although printing dense lines and trenches is more challenging for optical lithography, it is well-suited for imprint lithography; conversely, printing isolated lines with Step and Flash imprint lithography is difficult, whereas it is the easiest feature to print with optical lithography.[11,20]

Experimental Section

Materials. All chemicals were obtained from Aldrich and used without further purification unless otherwise noted. Dichloromethane was distilled under argon from calcium hydride. Methacryloyl chloride and triethylamine were distilled under argon. Analytical thin-layer chromatography (TLC) was performed on commercial Merck plates coated with silica gel GF254 (0.25 mm thick). Silica gel for flash chromatography was Merck Kiselgel 60 (230−400 mesh). Silicon wafers (1 in., <100>) were obtained from Virginia Semiconductor, Inc. 2,5-Dimethyl-2,5-hexanediol dimethacrylate was prepared according to a reported procedure.[26]

Instrumentation. Nuclear magnetic resonance (NMR) spectroscopy was performed on a Bruker Avance 400 spectrometer using the internal solvent peak as reference. Film thicknesses were calculated using the Gaertner Ellipsometer Measurement Program and delta and psi values obtained from a Gaertner Scientific Variable Angle Stokes Ellipsometer L116SF. Ellipsometry measurements were done at an angle of 70° with a wavelength of 632.8 nm. For the calculations, the N_s and K_s values for the silicon substrate were taken as 3.881 and −0.018, respectively. The silicon oxide layer was assumed to be 2.0 nm with a refractive index of 1.457, and the refractive index of the organic film was assumed to be 1.5. Thermogravimetric analysis was done on a TA Instruments TGA-2950 at a rate of 10 °C/min under a nitrogen atmosphere. Attenuated total reflection infrared (ATR-FTIR) spectra of thin films on silicon wafers were taken with a Nicolet Nexus 870 FTIR using a MCT detector and a Harrick Scientific Corporation GATR accessory. FT−IR spectra of thin films on KBr were obtained using the same Nicolet Nexus 870 FTIR, however with a DTGS detector. For all IR measurements, the sample chamber was purged with nitrogen to remove carbon dioxide and water peaks. A total of 32 scans were taken for each spectrum, and the spectra were referenced as was appropriate, either to a bare silicon wafer or an empty sample chamber.

Synthesis of 2,5-Dimethyl-2,5-hexanediol dimethacryl ate (DHDMA), 1.[26] A solution of 2,5-dimethyl-2,5-hexanediol (13.8 g, 94.2 mmol) and anhydrous triethylamine (31.6 mL, 226 mmol) in dichloromethane (490 mL) was prepared and cooled to 0 °C under argon. Methacryloyl chloride (21.7 g, 207 mmol) was added dropwise under argon. The mixture was allowed to slowly reach room temperature over 1 h and then stirred for 4 h. The mixture was washed five times with a solution of potassium hydroxide in water (pH ~8, 500 mL), dried with magnesium sulfate, and evaporated to dryness. The crude product was purified by flash chromatography, eluting with 95% hexane/5% triethylamine to yield the product, **1**, as a colorless liquid (16.4 g, 62%). Acidic conditions and temperatures above 50 °C should be avoided to prevent decomposition of the cross-linker, **1**. ^{1}H NMR: $((CD_3)_2C{=}O)$ δ 6.02 (s, 2H, $CH_2{=}$), 5.57 (s, 2H, $CH_2{=}$), 1.93 (s, 4H, CH_2CH_2), 1.91 (s, 6H, ${=}CCH_3$), 1.51 (s, 12H, $C(CH_3)_2$). ^{13}C NMR: $(CDCl_3)$ δ 167.0, 138.2, 124.8, 82.4, 35.2, 26.1, 18.6. IR (neat): 2978, 1713, 1636, 1473, 1369, 1332, 1175, 937 cm^{-1}.

Imprinting of DHDMA and DHDMA/Acetoxy Styrene Films. The stamp fabrication, substrate preparation, and imprinting procedures used were described by von Werne et al. and McClelland et al.[17,28] The acid-cleavable resins were prepared from a solution of monomer (either DHDMA or a 2:1 mass ratio of DHDMA to *p*-acetoxystyrene) (98%) and 2,2-dimethoxy-2-phenylacetophenone (2%) in propylene glycol methyl ether acetate (PGMEA) (varying amounts depending on concentration). The solution (0.2 mL) was then filtered through a 0.45 μm PTFE filter onto a wafer coated with a self-assembled monolayer of adhesion promoter (3-methacryoxypropyl trimethoxysilane) and spin-coated at 3000 rpm for 30 s. The stamp was then placed on top of the coated wafer followed

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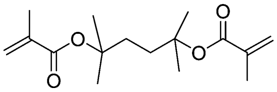


Figure 1. Structure of 2,5-dimethyl-2,5-hexanediol dimethacrylate (DHDMA), **1**.

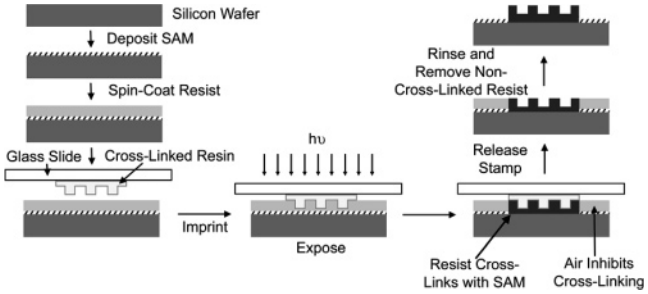


Figure 2. Process scheme for patterning with UV-IL system developed by McClelland et al.[17]

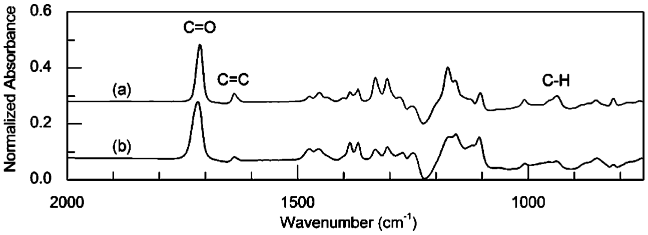


Figure 3. ATR-FTIR spectra of a DHDMA film (a) before and (b) after photopolymerization.

by a flat disc of PDMS on top of the stamp, and then an Instron 5500R and the associated Merlin software were used to apply a force that was ramped up to 400 N. After 30 s, the sample was exposed to 1000 mJ/cm^2 of 365 nm radiation (OAI Model 30 light source, 33 mW). The applied force was then removed from the sample, and the stamp was removed from the wafer. The wafer was then rinsed with acetone and isopropanol while being spun on a spin-coater and the unreacted resin was removed, giving the patterned wafer. Extraction experiments on both nonpatterned as well as imprinted wafers showed that less than 1−2 wt % of material was soluble after cross-linking.

Acid-Catalyzed Decomposition of DHDMA Cross-Linked Films. The imprinted layers were coated with a thin layer of polystyrene (6,000 g/mol, 10%) containing a PAG (bis(*tert*-butyl phenyl) iodonium triflate, 1%) by applying a PGMEA solution by spin-coating techniques (2,500 rpm for 60 s) to create a 214 ± 2 nm thick overcoat. The samples were exposed to 254 nm radiation (OAI Model 30 light source and a 254 nm filter, 0.74 mW), baked on a hot plate at 110 °C, and then rinsed with toluene and acetone, alternating two times with each, to remove the polymer layer and any decomposed film before being dried under a stream of nitrogen. The sample was then placed in a 28% solution of ammonium hydroxide for 5 min, rinsed with water and ethanol, and dried under a stream of nitrogen. To photolithographically pattern the DHDMA films, the same procedure was used; however, TEM grids (TED Pella, nickel, 1000 mesh) were placed on top of the PAG/PS film before exposure and removed before baking.

Thermal Decomposition of the DHDMA Cross-Linked Films. The thermal decomposition of DHDMA films was performed by heating of the wafers on a hot plate at 250 °C. The reaction was monitored in two ways: (1) a single sample was examined by ellipsometry and ATR-FTIR every 15 min and (2) eight samples were placed on the hot plate, with each one baked for different lengths of time, and the individual samples monitored by ellipsometry and ATR-FTIR both before and after development of the films with ammonium hydroxide. The thickness changes with time for samples prepared were identical, regardless of the monitoring strategy.

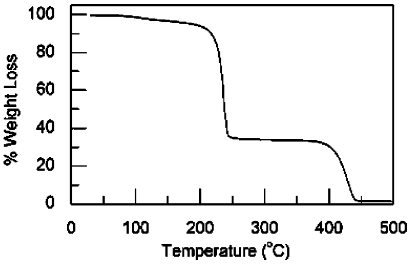
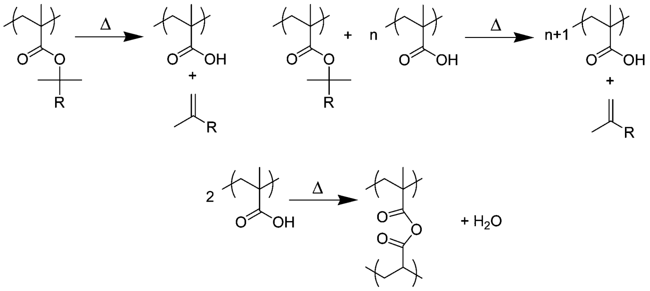


Figure 4. Thermogravimetric analysis of cross-linked DHDMA.

Scheme 1. Proposed Chemical Reaction for the Thermal Decomposition of the DHDMA Linkages[31,35]



Polymerization of DHDMA for TGA. A solution of DHDMA (49 wt %) and benzoyl peroxide (1 wt %) in benzene was prepared and placed in an ampule. After three freeze−thaw cycles, the ampule was sealed under a vacuum and placed in an oil bath at 60 °C for 30 min. The ampule was then removed; after being washed repeatedly with acetone, the gel was dried under a vacuum to remove any residual solvent before we performed TGA analysis.

Results and Discussion

In developing an acid-cleavable cross-linker for imprint lithographic applications, two important characteristics are fast polymerization times and an acid sensitivity comparable to that of chemically amplified resists. Traditionally, UV-IL resists have been based on functionalized acrylates or methacrylates because of their efficient photopolymerization,[24] whereas acid-cleavable groups in photoresists are typically tertiary esters, carbonates, or acetals.[11,12] As a result, our initial goal was to examine the development of dimethacrylate or diacrylate cross-linkers containing acid-sensitive tertiary esters with 2,5-dimethyl-2,5-hexanediol dimethacrylate, **1** (DHDMA, Figure 1). Previously, **1** has been used in the creation of acid-decomposable networks through the pioneering work of Ober[25] and Long,[26] with applications in degradable thermoset epoxies,[25] as well as in the creation of acid-labile cores for star polymers.[26] Additionally, Li et al. reported promising results in the use of a similar acid-cleavable cross-linker for imaging applications with a chemi-

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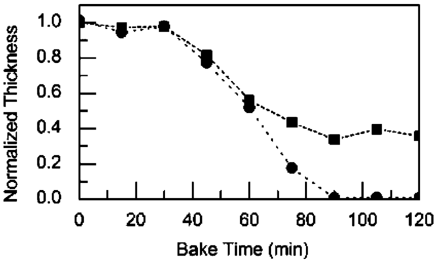

Figure 5. Thickness change of a DHDMA cross-linked film baked at 190 °C before (■) and after (●) development with ammonium hydroxide.

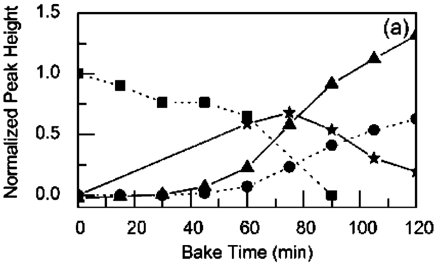

Figure 6. Normalized peak heights from ATR-FTIR spectra of DHDMA cross-linked films after being heated at 190 °C and rinsed with acetone: (■) ester, 1716 cm^{-1}; (▲) anhydride, 1803 cm^{-1}; (●) anhydride, 1760 cm^{-1}; (★) carboxylic acid, 1704 cm^{-1}.

cally amplified mechanism; however, cross-linker concentrations were low (2%) and the resolution of this system was not explored.[27] In examining the compatibility of the resists based on DHDMA for UV-IL applications, we explored the resolution of this system both with imprint techniques as well as with optical lithography. Thin film characterization techniques were also used to examine and compare the decomposition of the film by both thermal and acid-catalyzed mechanisms.

Imprinting of DHDMA. The imprinting system and stamp compositions used were developed by McClelland et al.[17] (Figure 2) and are characterized by a soft stamp backed by a glass slide, which is compatible with rough substrates; it is also simple to manufacture from a silicon master. The substrates used in this system are silicon wafers, treated first with a piranha etch to oxidize the surface and second by deposition of a self-assembled monolayer (SAM) of 3-methacryloxypropyl trimethoxysilane. The resist, composed of DHDMA (98%) and a photoinitiator (2,2-dimethoxy-2-phenylacetophenone, 2%), is then applied by spin-coating, and the film is imprinted using a force of 400 N while being exposed to 365 nm radiation.

When compared to a typical resist used with UV-IL systems, a mixture of *N*-vinyl pyrrolidinone (18.5%), trimethylolpropane triacrylate (18.5%), and ethoxylated bisphenol A-dimethacrylate (61%),[28] the DHDMA resist has similar processing characteristics. For example, DHDMA is a high-boiling-point material, so does not evaporate during spin-coating; its viscosity also approaches that of the mixture described above, which allows for spin-coating of films approaching thicknesses of 1 μm. In addition, this resist does not dewet the substrate before imprinting and releases easily from the stamp after cross-linking. The exposure doses required to imprint both resist systems are identical, 1000 mJ/cm^2, indicating that both polymerize at comparable rates. These similarities suggest that DHDMA can be used in imprint lithography under situations similar to those of traditional UV-IL resists while allowing for the increased functionality and versatility of having an acid-cleavable cross-linker.

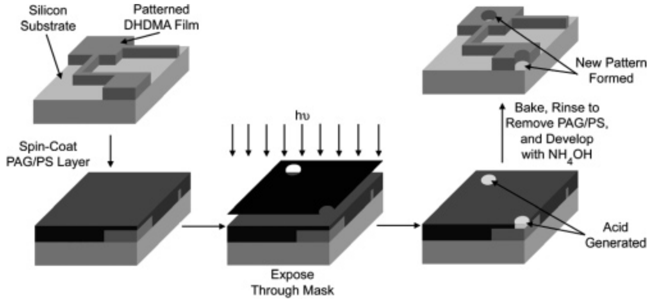

Figure 7. Graphical representation of process for patterning cross-linked films of DHDMA using photogenerated acid.

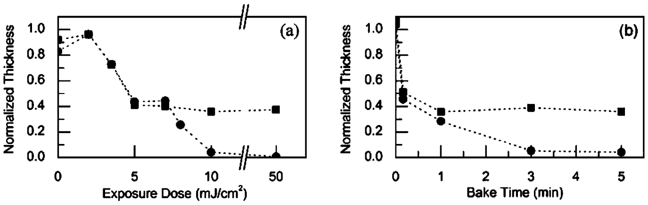

Figure 8. Thickness changes for undeveloped (■) and developed (with ammonium hydroxide) (●) cross-linked DHDMA films coated with a PAG supply layer and then processed for (a) varying exposure doses with 5 min of postexposure bake at 110 °C and (b) varying postexposure bake times at a temperature of 110 °C with an exposure dose of 10 mJ/cm^2.

Characterization of Cross-Linked DHDMA polymers. A critical aspect of the incorporation of acid-degradable cross-links is the stability and fidelity of the cleavage chemistry and the extent of reaction for both methacrylate groups, which leads directly to the extent of cross-linking. To determine the effect of photopolymerization on the thin films and the absence of nondegradable cross-links, we initially examined films of DHDMA with attenuated total reflection FTIR (ATR-FTIR) spectroscopy before and after UV exposure and development (Figure 3). Only minor changes were observed on photopolymerization, with the expected decrease in absorbance due to the C=C stretching vibration at 1637 cm^{-1} and C−H out-of-plane deformation at 937 cm^{-1}. However, one important observation is that the vinyl peaks do not disappear with ca. 50% of the absorbance due to the vinyl groups remaining.[29]

To further investigate the extent of cross-linking, we studied the thermal decomposition of bulk cross-linked thin films of DHDMA by thermogravimetric analysis (TGA) and compared the weight loss due to decomposition of the tertiary ester linkages with theoretical values for full cross-linking and no cross-linking (model linear polymer) (Figure 4). If the network was 100% cross-linked, decomposition of every ester linkage and the subsequent release of 2,5-dimethyl-

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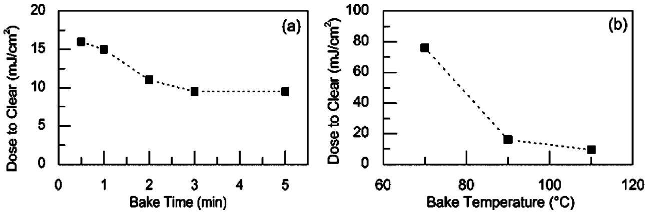

Figure 9. Dose to clear as a function of (a) heating time at 110 °C and (b) temperature for a bake time of 5 min for cross-linked DHDMA films.

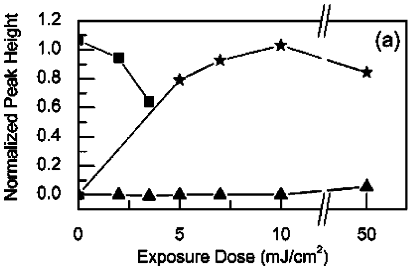

Figure 10. Normalized ATR peak heights for DHDMA cross-linked films after baking at 110 °C for 5 min and rinsing with acetone: (■) ester, 1716 cm^{-1}; (▲) anhydride, 1803 cm^{-1}; (★) carboxylic acid, 1704 cm^{-1}.

1,5-hexadiene would correspond to a 39% weight loss. In addition, under the thermal analysis conditions, methacrylic acid units frequently react to form anhydride cross-links, which would increase the weight loss to 45%, assuming complete anhydride formation. At the opposite end of the spectrum, no cross-linking would lead to a linear polymer whose decomposition involves loss of both 2,5-dimethyl-1,5-hexadiene and methacrylic acid. As a result, linear structures would give rise to a weight loss of 73%, assuming anhydride formation. Experimentally, a smooth decomposition profile is observed with initial weight loss occurring between 215 and 245 °C, which is similar to that observed for poly(*tert*-butyl methacrylate) (PTBMA).[30,31] More significantly, the actual weight loss of 60% falls approximately midway between these extremes of 45 and 73 wt %, providing further support for the bulk DHDMA materials being ca. 50% cross-linked. This result is expected, as the pendent vinyl groups are known to have decreased reactivity when compared to that of monomers; also, steric constraints restrict reaction as the network develops, leading to incomplete polymerization in the DHDMA cross-linked structure.[32,33]

Thermal Decomposition of Cross-Linked DHDMA Films. Having demonstrated the overall decomposition profile for DHDMA based materials, we obtained functional group and thin film profiles for cross-linked thin films prepared with UV-IL. Flat films of DHDMA were prepared and heated at 190 °C, with thickness and chemical changes monitored by ellipsometry and ATR-FTIR. During heating, the ester linkages thermally decompose and release 2,5-dimethyl-1,5-hexadiene, which has a boiling point of 114 °C[34] and therefore evaporates, reducing the film thickness (Scheme 1). After 90 min, the 2,5-dimethyl-1,5-hexadiene has been completely released and a minimum film thickness of approximately 40% of the initial thickness is reached (i.e., 60% reduction). Of particular note is the correlation of this thickness change with the observed weight loss of 60% and the complete dissolution of the film when developed with ammonium hydroxide (Figure 5).

The chemical changes during decomposition of the DHDMA films, including ester linkage cleavage and anhydride formation, were monitored by ATR-FTIR and show trends identical to the decomposition chemistry of PTBMA (Figure 6).[36] As the ester linkage decomposes, carboxylic acid groups are formed and the alkene is released. After about 45 min at 190 °C, when the concentration of carboxylic acid groups reaches a critical level, anhydride linkages are formed, with complete loss of the original ester groups after 90 min. A consequence of the formation of high concentrations of anhydride cross-links is the insolubility of the thin films; however, simple treatment of these films with aqueous ammonium hydroxide solution results in cleavage of the anhydride cross-links and complete dissolution of the resulting linear polymers.

Acid-Catalyzed Decomposition of Cross-Linked DHDMA Films. As with photoresists based on tertiary ester or carbonate linkages, the addition of acid to the cross-linked DHDMA films dramatically speeds up the deprotection reaction. The rate-limiting step in this reaction has been shown to be the decomposition of the protonated carbonyl in the ester linkage, whereas the protonation reaction is very fast.[31] Thus the concentration of acid that is delivered to the film is very important in controlling the decomposition of the film. For the DHDMA films, acid was delivered by spin-coating a layer of 10% photo-acid generator (PAG) in polystyrene (PS) on top of the films and then exposing it to deep-UV radiation (254 nm) followed by thermal baking (Figure 7).[37] By exposing the films to varying doses of deep-UV radiation (254 nm), we can generate different concentrations of acid in the polymer film; during the subsequent bake step, the acid diffuses into the DHDMA film, cleaving the ester linkages. Rinsing with acetone and toluene removes the PS film and any 2,5-dimethyl-1,5-hexadiene that is present. Finally, developing in ammonium hydroxide cleaves thermally induced anhydride cross-links and removes the exposed poly(methacrylic acid) regions.

To compare the acid-catalyzed decomposition of DHDMA to the thermal decomposition, we examined the effect of exposure dose and bake time. Figure 8a shows the decrease in DHDMA film thickness as the exposure dose is increased, indicating a dose to clear of 10 mJ/cm^2 for a bake step of 5 min at 110 °C. The trend for this acid-catalyzed decomposition matches that of the thermal decomposition, in particular the initial delay before decomposition begins (Figure 8). As with the thermal decomposition results, acid-catalyzed depro-

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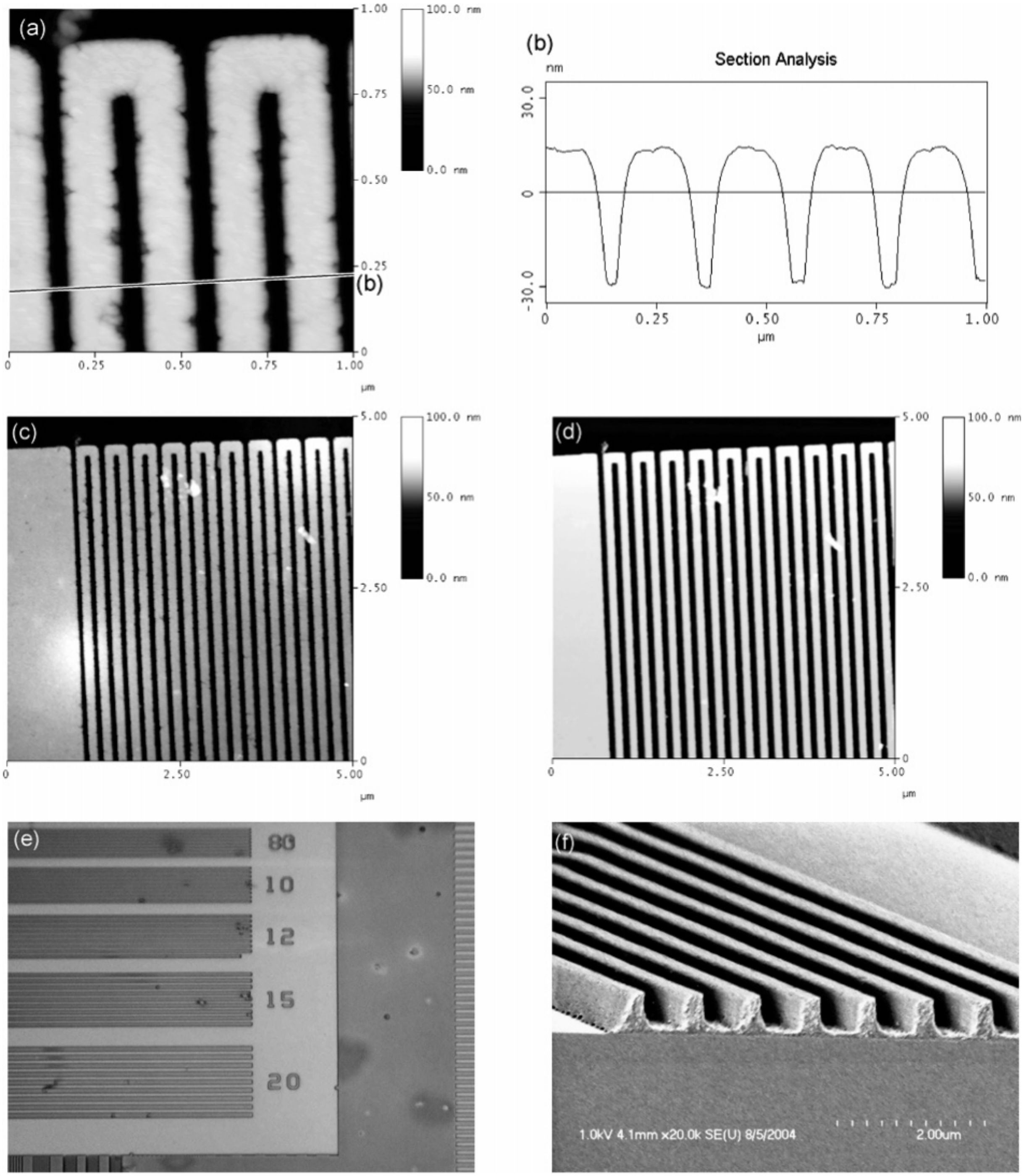

Figure 11. Characterization of DHDMA imprinted films. AFM images of 130 nm lines with a 45 nm height: (a, b) 1 *µ*m scan and corresponding section analysis; (c) 5 *µ*m scan and (d) 5 *µ*m scan of the corresponding master. (e) Optical microscope images of 0.8−2.0 *µ*m lines. (f) Cross-sectional SEM image of 150 nm lines.

tection of cross-linked DHDMA shows decomposition behavior similar to that of a linear polymer with a comparable acid-sensitive linkage (PTBMA).[38]

When the bake time is varied while the dose (10 mJ/cm^2) and bake temperature (110 °C) are held constant, the film thickness can be observed to decrease with time, until after 3 min, when the film has undergone complete reaction (Figure 8). When compared to the thermal decomposition of the film, which required 90 min of heating at 190 °C, this rate of reaction is significantly higher, even at a much lower temperature. Significantly, the shape of the thickness vs bake time curve is similar in shape to that of PTBMA,[31] with the film thickness decreasing quickly over the initial few seconds of bake time, before slowing significantly and approaching zero over several minutes.

To pattern the DHDMA films with the highest possible resolution, we determined the dose to clear for a range of bake times and temperatures. As shown in Figure 9, with the bake temperature held constant at 110 °C, the dose to clear decreases with increasing bake time up to 3 min. At that point, the curve levels off, with longer bake times

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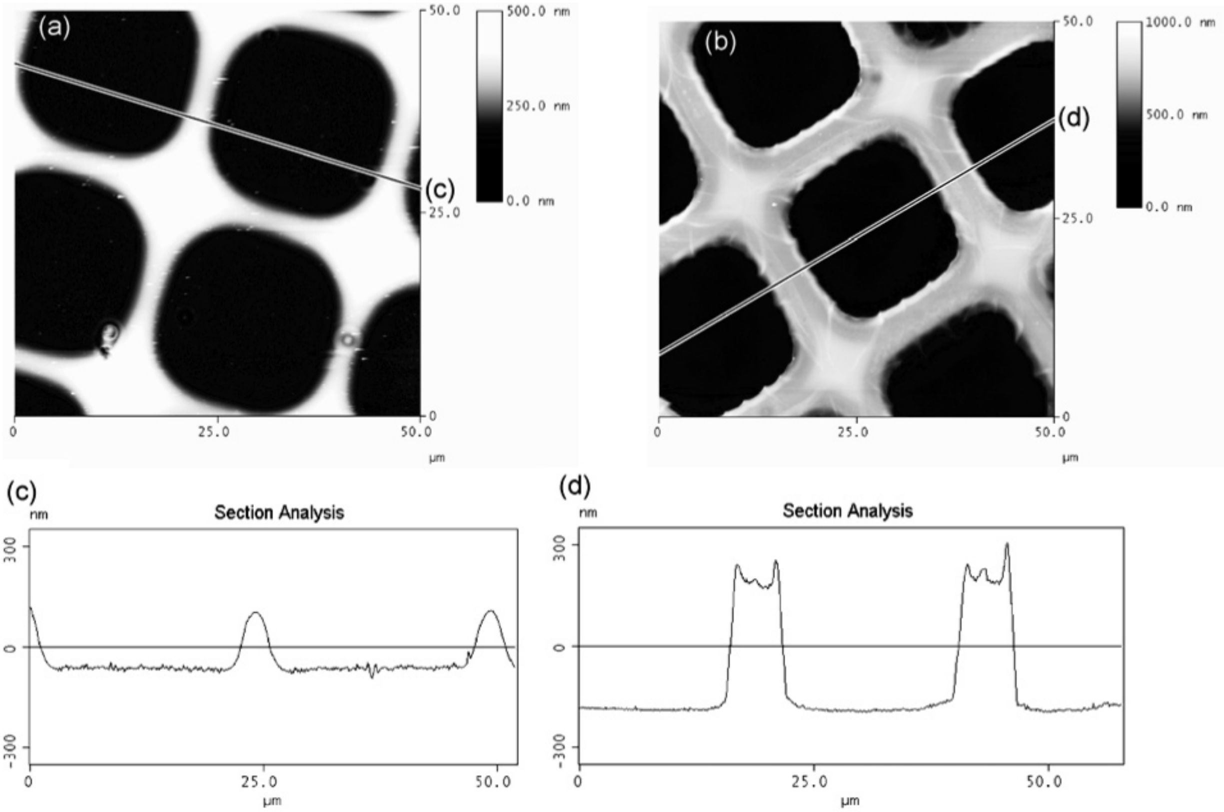

Figure 12. AFM images (50 μm scans) and corresponding section analyses of flat cross-linked DHDMA films lithographically patterned with varying exposure doses: (a, c) 5 mJ/cm^2 (underexposed); (b, d) 150 mJ/cm^2 (fully exposed).

requiring identical doses to clear. This trend likely has the same origin as the tapering-off of the thickness vs bake time curve, with the concentration of acid in the film decreasing over the course of the bake step (Figure 8).

When the effect of bake temperature on dose to clear is examined, a much larger variation is observed, with the dose to clear increasing from 10 to 75 mJ/cm^2 when the temperature is reduced from 110 to 70 °C (Figure 9). This feature allows for the incorporation of heat-sensitive functional groups, such as alkoxyamine initiators, into the film by using a combination of high doses and low bake temperatures. The effect of a reduced bake temperature and time (5 min at 110 °C) on the chemistry occurring during patterning of these films was then monitored by ATR-FTIR. As shown in Figure 10, the concentration of ester linkages decreases sharply with increasing exposure dose, while the concentration of carboxylic acid groups concomitantly increases. However, one significant difference with the purely thermal process is the complete absence of anhydride linkages up to a dose of 10 mJ/cm^2. Only at large doses (50 mJ/cm^2) were minor concentrations of anhydride groups observed, which was again accompanied by a slight decrease in the concentration of carboxylic acid groups.

Imprinting of DHDMA Films. Having demonstrated the acid-catalyzed decomposition of DHDMA cross-linked thin films and defined a suitable processing window, we investigated nanoimprinting and secondary lithographic patterning of these thin films using stamps with a wide range of feature sizes and shapes. The imprinted films were characterized by a combination of optical microscopy, atomic force microscopy (AFM), and scanning electron microscopy (SEM). As can be seen in Figure 11, DHDMA could be easily imprinted over large areas (approximately 10 cm^2), while simultaneously patterning features in a variety of shapes and length scales, from tens of micrometers to sub-100 nanometers (panels a and b of Figure 11). The smallest imprinted features were 130 nm lines with a height of 45 nm (panels c and d of Figure 11); however, these images also contain replications of defects from the stamp that are on the order of 10 nm. The irregularities that appear in the AFM images are materials-related defects and likely due to shrinkage during cross-linking, which could be improved by the addition of comonomers. The cross-sectional SEM image of 150 nm lines demonstrates one of the characteristics of imprint lithography, a thin residual layer that appears between the imprinted features, the thickness of which depends on the thickness of the initial spin-coated film (Figure 11f). In this case, the film is only present between the dense lines and spaces and not in the large open areas, which is due to accurate control over initial film thickness and the flow of the material away from open areas.

Patterning of Stamped DHDMA Films. The successful application of DHDMA as a high-resolution UV-IL resist now opens up a range of new features and possibilities for cross-linked imprinted films through secondary lithographic steps. The large processing window observed for DHDMA allows the selective generation of acid by initially coating the DHDMA cross-linked films with a layer of polystyrene-containing PAG and then exposing the films through a mask, thereby generating acid in only the exposed areas. For these experiments, the masks used were TEM grids whose structural features were 20 μm squares. The bake conditions

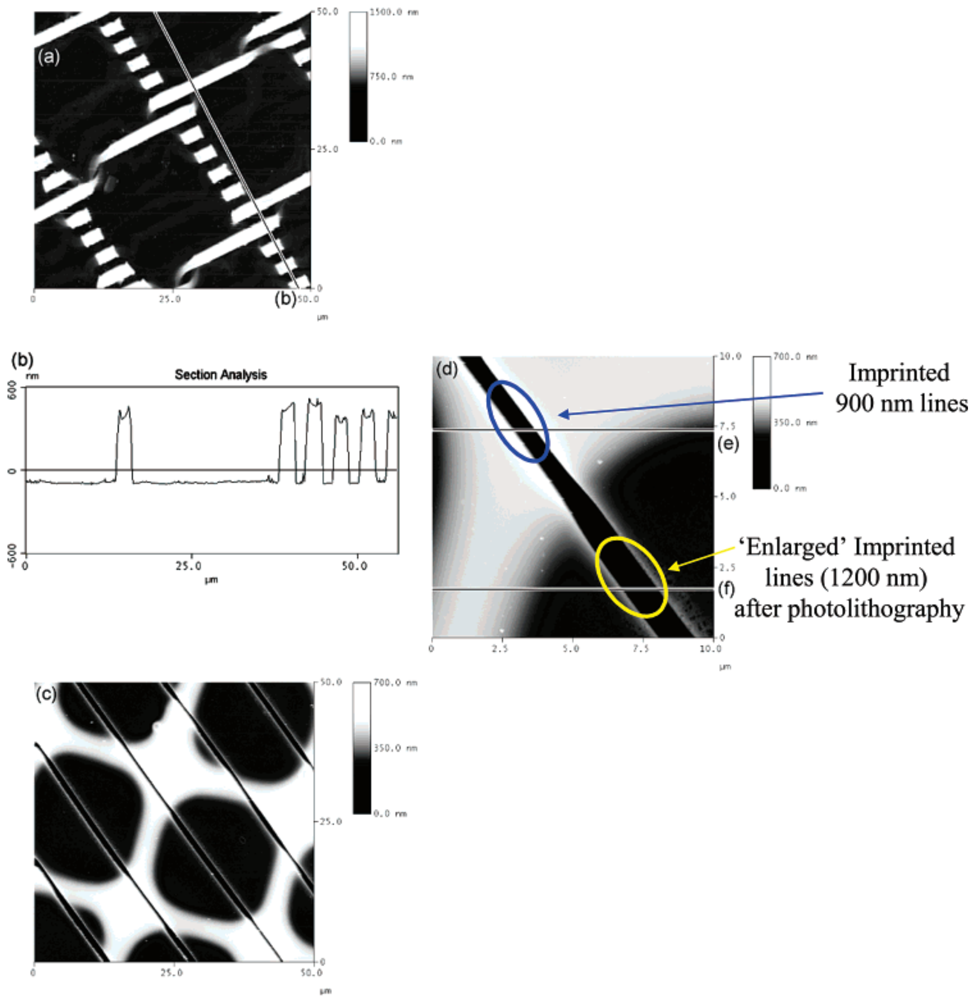

Figure 13. AFM images and corresponding section analyses of imprinted cross-linked DHDMA films lithographically patterned with varying exposure doses: (a, b) 150 mJ/cm^2 (fully exposed, 50 μm scan); (c, d) 5 mJ/cm^2 (underexposed and 10 and 50 μm scans).

were 110 °C for 1 min, and the dose ranged from 5 to 150 mJ/cm^2. Shown in Figure 12 are AFM images containing examples of the patterns that are created using this technique with flat, nonpatterned DHDMA films with either underexposed (5 mJ/cm^2) or full exposure (150 mJ/cm^2). As expected from the results above, exposure to a dose lower than the dose to clear results in a thickness change of only 200 nm for a film 500 nm thick compared to exposure to the dose to clear in which all of the cross-linked polymer (500 nm) is removed.

The versatility of these DHDMA films can be fully realized if this chemically amplified photolithography is combined with imprint lithography to create secondary patterns, including the formation of three-dimensional features (Figure 13). When the films are fully exposed (150 mJ/cm^2) and a mask is used that contains features larger than the imprinted features (2.5 μm lines), a pattern is formed in which the smaller imprinted features appear in the shape of the mask. Interestingly, the underexposure of these films (5 mJ/cm^2) results in a three-dimensional topography in which the imprinted trenches have a height of 500 nm, and the photolithographically exposed areas are reduced in thickness by 200 nm. This image also provides insight into the effect of performing lithography on patterned features. Because the polystyrene/PAG film fills the imprinted trenches during spin-coating, acid is generated inside these features during exposure, resulting in a widening of the trenches in the exposed areas. In this case, the width changed from 900 to 1200 nm (+300 nm), approaching the expected 400 nm change (2 × thickness change).

Conclusions

An acid-cleavable cross-linker, 2,5-dimethyl-2,5-hexanediol dimethacrylate (DHDMA), has been developed that is compatible with UV-IL systems, both in physical properties such as wetting behavior and viscosity and in reactivity during polymerization. Incorporation of this cross-linker into resists for UV-IL allows for decomposition of the cross-links and permits lithographic patterning that allows for the fabrication of films with three-dimensional topography in a range of feature sizes, from nanometer to micrometer scale. Such properties are not limited to DHDMA homopolymer, but are retained during the imprinting of copolymers of DHDMA with other vinyl monomers, allowing for the potential extension of this system to a range of different applications by the use of functionalized monomers. The use of DHDMA in UV-IL systems improves the versatility of the imprinted films by removing the need for use of potentially damaging etches in the removal of the cross-linked films and extending the range of patternable features by combining the benefits of both imprint and optical lithography.

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