Additively Patterned Polymer Thin Films by Photo-Initiated Chemical Vapor Deposition (piCVD)

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Patterned micro- and nanoscale structures in thin films are the basic building blocks of the traditional semiconductor industry[1] and more recently for organic electronics,[2] flexible displays,[3] and optical waveguides.[4] Additionally, patterned thin films have utility in both basic biological studies[5] and bioimplantable materials design.[6,7] Microstructure patterns on the surface of biomaterials can be used stimulate cell recognition and adhesion,[6] complementary to surface functionalization with chemical signals.[7,8]

The traditional method of subtractive patterning relies on the deposition of blanket films from which region layers of material which are selectively removed.[9] This requires application of a resist layer which is patterned through selective irradiation and development. Next the pattern is transferred to underlying layer, followed by stripping of the remaining resist. This process is slow, wasteful, and environmentally unfriendly because of the large volumes of solvent involved.[10,11] Conversely, additive patterning deposits film only in the desired regions, eliminating the need for a resist and the associated processing steps.

Additive processing of polymeric films by chemical vapor deposition (CVD) has been demonstrated by Yasutake et al. using heated substrates to activate prepatterned initiators on the surface.[12] Another example of additive deposition employed blanket deposition of surface tethered initiators which are selectively activated by irradiation through a photomask.[13] However, only limited thicknesses were achieved by this second approach even after a long deposition period (24 h).

The methodology described in this communication allows the substrate to be maintained at low temperature, an advantage for biological applications involving temperature sensitive substrates. Additionally, spatial selectivity is achieved through blanket radiation on a patterned photoinitiator rather than patterned radiation on a blanket initiator. As a result, the deposition of patterned films >100 nm is achieved at reasonable rates, most likely as a result of the improvement in selectivity achieved by avoiding the presence of initiator outside the patterned region. In addition, this work is the first example of additively patterned vapor deposited polymer films using soft lithography.

In the current work, a free radical generating photoinitiator is first patterned onto a substrate using microcontact printing. This substrate is then exposed to UV irradiation in the presence of a vaporized monomer in a process termed photoinitiated CVD (piCVD). Cyclohexyl methacrylate (CHMA) has been selected as the monomer and benzophenone (BP), or its derivative Michler's Ketone (MK), as the photoinitiator. Previous work, demonstrating both deposition of poly(cyclohexyl methacrylate) (pCHMA) by initiated CVD (iCVD)[14,15] and the piCVD of other monomers with BP,[16] inspired this selection of model system. pCHMA is an excellent sacrificial material, and patterned films of this polymer have been utilized in the formation of air gap structures.[15] The method is quite general and could deposit patterned films of any polymer that can be synthesized by iCVD including poly(glycidyl methacrylate),[17] poly(hydroxyethyl methacrylate),[18] and poly(trivinyltrimethylcyclotrisiloxane).[19]

To facilitate microcontact stamping, solutions of photoinitiator in acetone were utilized. Acetone was selected as the solvent to achieve both high concentrations of the selected photoinitiators and rapid drying times. BP and MK are type II free radical initiators which can be activated with both 254 and 365 nm wavelength UV photons.[20] In addition, the low vapor pressure of these initiators (<3 mTorr at 298 K)[21] allows samples to be placed under vacuum without expectation of initiator pattern evaporation. Multiple initiator concentrations were examined, although best results were generally obtained at the highest possible (saturation) concentration. Initiator solutions were applied to the surface

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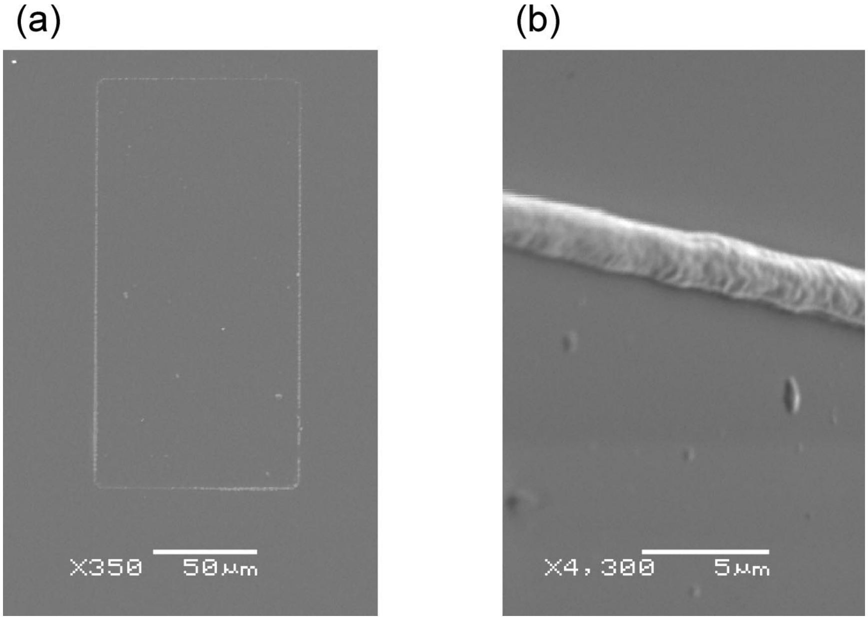

Figure 1. Scanning electron micrographs (SEMs) showing patterned deposition of p(CHMA) following microcontact printing of BP/acetone solution. Panel a depicts the outline of a 100 μm × 200 μm rectangle, and panel b is an enlargement of one edge of the deposited structure.

of a PDMS stamp using a cotton swab. The stamp was either immediately contacted to the deposition surface or first dried completely with room temperature nitrogen. All depositions were performed on silicon wafer substrates. These wafers were either utilized without modification or surface modified with trichlorophenylsilane, for the surface presentation of phenyl groups, prior to initiator stamping.

When a microcontact stamp, wet with a BP–acetone solution, was applied to an unmodified substrate, subsequent patterned piCVD p(CHMA) polymer growth is evident only at the feature's outline. This "coffee stain" effect, observed in inkjet printing of microscale features,[3,22] results from concentration of the BP solution during evaporative drying of the acetone. Retention of pattern edge fidelity occurs due to surface tension and wetting effects which dictate that the evaporative front move from the center of the wetted area to the edge.[23] The intentional use of this phenomenon to create patterns, known as edge transfer lithography (ETL), has been shown to allow the transfer of smaller features than traditional microcontact printing.[24] While a resolution of 2–3 μm is achieved (Figure 1b), reproducibility is difficult, leading to lack of regularity in the outline (Figure 1a).

No deposition was observed when the microcontact stamp was dried with nitrogen prior to contacting the substrate. Instead, the BP crystallized on the surface of the stamp which likely prevented the transfer of any initiator to the substrate, regardless of whether or not the substrate was modified with trichlorophenylsilane.

Figure 2 displays an optical micrograph of the patterned deposition resulting from the piCVD of CHMA on a trichlorophenylsilane modified substrate to which a microcontact stamp, wet with a MK–acetone solution at a saturation concentration of 2.2% by weight, was applied after drying with nitrogen. Patterned deposition now occurs over the full area of the stamped feature. As anticipated from its chemical properties, the MK was not observed to crystallize on the stamp. Transfer to the substrate during contacting was due to favorable interactions with phenyl modified surface as unmodified substrate resulted in no deposition.

The features shown in Figure 2a have a thickness of 25–30 nm, as measured by profilometry, corresponding to a deposition rate of 0.5 nm/min. To achieve thicker patterned films, a substantial increase in deposition rate was required. The rate of iCVD growth is known to increase with the partial pressure of the monomer within the iCVD deposition chamber[14,25,26] However, when CHMA partial pressure was increased from 250 mTorr to 300 mTorr under 254 nm UV illumination, patterned film growth was no longer observed. Instead, a continuous CHMA film was deposited on the substrate, with no observable differentiation between areas patterned with photoinitiator and those without. It is theorized that the higher surface concentration of CHMA allowed for autopolymerization under the 254 nm UV irradiation. To avoid this nonselective deposition, the wavelength of irradiation was increased to 365 nm. This less energetic wavelength, while still activating the MK present on the surface, did not initiate autopolymerization of the monomer even at a partial pressure of 300 mTorr. This allowed for selective deposition of patterned films with 25 μm features at thicknesses of 100 nm, as measured by profilometry, in 45 min of deposition time (Figure 2b). This is a substantial increase in growth rates from those observed by Andou et al. using tethered photoinitiators, which required 24 h to deposit 20–25 nm of film.

Figure 3 displays Fourier transform infrared spectroscopy (FTIR) of an additively patterned p(CHMA) film, a

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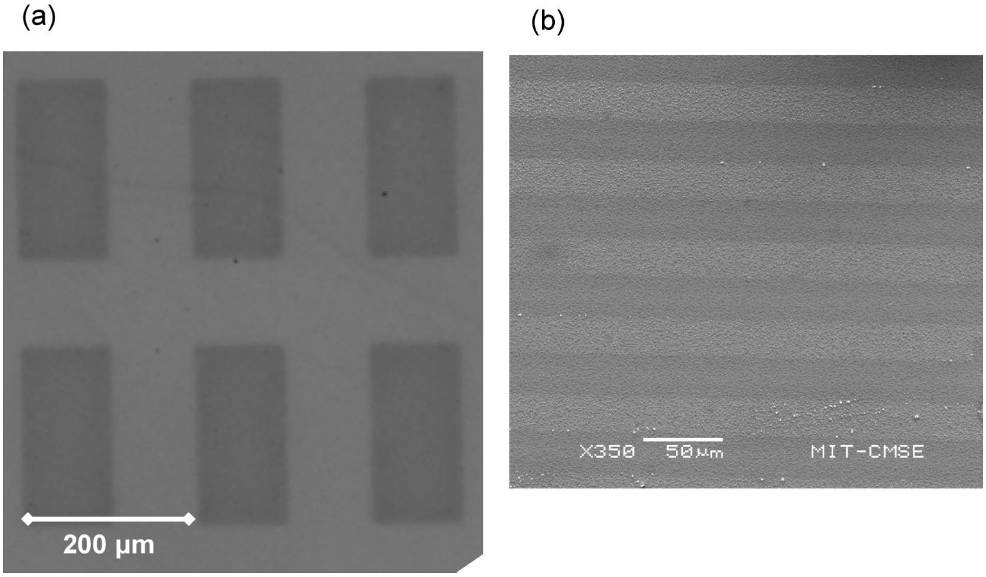

Figure 2. (a) Optical micrograph of 100 μm × 200 μm features deposited through piCVD of CHMA from microcontact patterning of the MK initiator. The feature area is fully filled in while deposition is not apparent outside of initiator patterned area. (b) SEM of 25 μm lines and spaces deposited to a film thickness of ~100 nm.

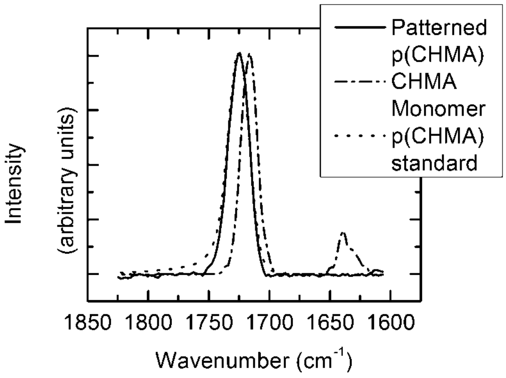

Figure 3. FTIR spectra in the 1600 cm^{-1} to 1875 cm^{-1} region of a patterned p(CHMA) film and a p(CHMA) standard are essentially identical, and both display a loss of vinyl moieties and a shift in carbonyl peak location relative to the CHMA monomer, confirming that polymerization has occurred.

p(CHMA) standard, and the CHMA monomer. The monomer spectra display two absorptions, one centered at 1635 cm^{-1}, indicative of the C=C stretch of an unsaturated vinyl moiety and the carbonyl stretch at 1716 cm^{-1}. Within the 1600 cm^{-1} to 1875 cm^{-1} region shown, both the patterned film and the p(CHMA) standard display only a single, identical absorption at 1725 cm^{-1}. This absorption is characteristic of the C=O bond of the carbonyl group.[27] Both the 9 cm^{-1} shift in location of the carbonyl peak and loss of the vinyl peak are clear evidence that polymerization has occurred.

Figure 4 displays high resolution C 1s X-ray photoelectron spectroscopy (XPS) scans for both a patterned p(CHMA) film and a p(CHMA) standard. Both spectra contain two distinct peaks, one associated with the carbonyl carbon located at 286.3 eV and another associated with the methyl and methylene carbons located at 282.5 eV. No other carbon peaks are present in the patterned polymer spectrum. These XPS data, along with the FTIR data presented above, provide strong confirmation that the patterned material is p(CHMA).

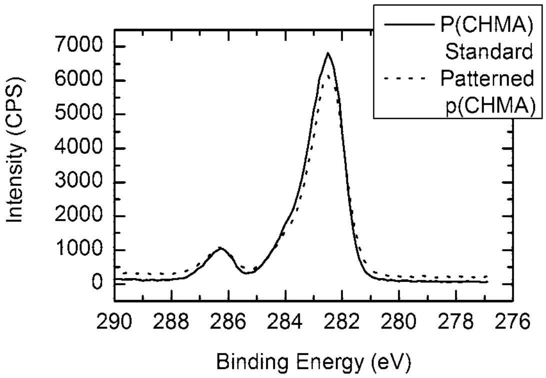

Figure 4. The C 1s XPS for both a patterned p(CHMA) film and for a p(CHMA) standard.

In this work, the additive patterned deposition of piCVD p(CHMA) films from a microcontact printed photoinitiator has been demonstrated. Utilization of this patterning technique was shown to require transfer of photoinitiator from the stamp surface by preventing initiator crystallization and optimizing surface preparation. Patterned deposition of p(CHMA) also required the use of a reduced energy UV wavelength, 365 versus 254 nm. Future work with this technique will focus on the creation smaller patterned features. In addition, alternate monomers such as glycidyl methacrylate of pentafluorophenyl methacryalte will be utilized to deposit patterned thin films of functional polymers for biological applications.

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