

Use of Microcontact Printing for Generating Selectively Grown Films of Poly(*p*-phenylene vinylene) and Parylenes Prepared by Chemical Vapor Deposition

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Several non-photolithographic methods for growing patterned films of parylene-based polymers prepared by chemical vapor deposition are presented. These patterns were generated using transition metals and metal salts known to inhibit polymer deposition, in combination with alkanethiols deposited by microcontact printing. By patterning the alkanethiols on gold or silver surfaces, well-defined selectively grown structures of vapor-deposited parylene-N and parylene-C were realized, with lateral dimensions ranging from 1.5 to 35 μm . Using carboxylic acid-terminated alkanethiols deposited by microcontact printing to define regions of iron salt exposure on the surface, selectively grown films of poly(*p*-phenylene vinylene) were generated, with features having lateral dimensions of 12.5 μm separated by 2.5 μm , and thicknesses of 750 Å. The structures fabricated with this approach have dimensions relevant to applications in microelectromechanical systems and polymer-based displays.

Introduction

Emerging applications for thin polymer films in electronic and optoelectronic devices, such as the conducting and insulating layers in integrated circuits (ICs)^{1,2} and thin film transistors (TFTs),^{3,4} or the active elements in light emitting diodes (LEDs),^{5,6} lasers,^{7,8} and photodiodes,^{9,10} often require spatial confinement of the organic layer. Such spatial definition can present many design challenges, since typical processing technologies for thin polymer films generate continuous sheets of material. Control and optimization of the macroscopic structure of thin polymer layers on surfaces have mainly been limited to postdeposition methods such as reactive ion etching^{11,12} developed for patterning thin films of inorganic materials. The harsh environments typical of these approaches can have undesirable side effects on the polymer, such as roughening of the surface, redeposition of the polymer on

the substrate, or degradation of the polymer integrity.² Patterning of polymers by direct photolithography has also been reported, but the method is limited to photo-sensitive chemistries.^{13,14} More recently, there has been a considerable amount of interest in ink-jet printing technology for spatial definition of solution-processed polymers used as the active element in organic-based LEDs.^{15–17} Although this technique avoids potentially destructive mechanical patterning of the organic material, it is serial in nature, and the edge definition and uniformity of the features are limited by the surface tension of the polymer solution.

An alternative approach to these technologies that has potential for controlling the structure of polymer films on the micron scale is selective deposition driven by localized differences in the chemical environment on the surface. For solution-processed polymers, soft lithography (in particular, microcontact printing (μCP)), can be used to direct the deposition of polymers on a substrate. In μCP , small molecules are transferred to localized regions of a substrate (typically alkanethiols deposited onto silver or gold) with a topographically patterned surface (or stamp). This approach offers a considerable amount of flexibility in tailoring the chemical environment and topography of the surface, since the end group functionality, length, and spatial geometry of the deposited organic molecules can be designed to fit specific needs. Micron-scaled spatial control of processes such as phase-separation of polymers,¹⁸ surface-initiated ring-opening metathesis polym-

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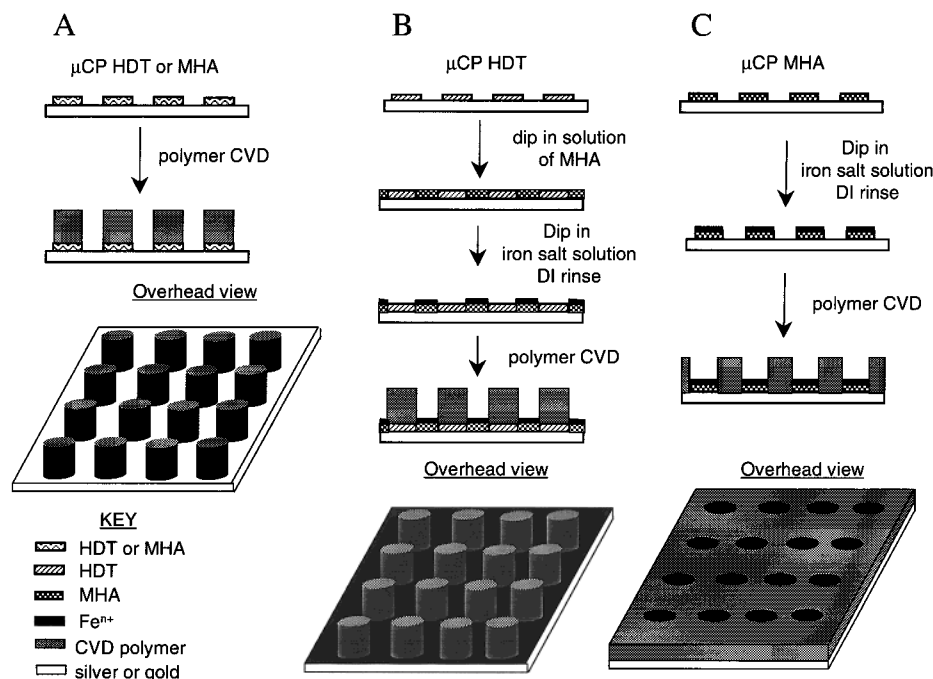


Figure 1. Use of μ CP to control the growth of CVD parylenes and PPV through (A) activation of the surface to polymer growth by μ CP of HDT or MHA, (B) deactivation of the printed regions of the surface to polymer growth by μ CP of MHA followed by exposure to an iron salt solution and rinse step, and (C) deactivation of the unprinted regions of the surface to polymer growth by μ CP HDT on the surface, depositing MHA on the unprinted regions, and exposing the entire surface to a solution of iron salt, followed by a rinse step.

erization,¹⁹ selective deposition of polyelectrolytes by sequential self-adsorption,²⁰ electroless deposition,²¹ and electrodeposition²² of conducting polymers have been achieved using surfaces patterned by μ CP.

Recently, we reported a novel method for realizing selective growth of parylene and its derivatives prepared by chemical vapor deposition (CVD).^{23,24} Specifically, we have discovered that deposition of the electroluminescent (EL) polymer poly(*p*-phenylene vinylene) (PPV), as well as parylene-N and parylene-C all prepared by CVD, is inhibited by several transition metals, metal salts, and organometallic complexes, such as those based on iron, ruthenium, platinum, palladium, silver, copper, and gold. (PPV is of interest for use in polymer-based LEDs⁵ and lasers,⁷ and the parylenes are of interest for multi-levelled ICs¹ and biopassivation coatings.²⁵) Although the exact mechanism by which inhibition occurs is not known, our studies suggest that the effect of the metal is to deactivate the *p*-xylylene reactive intermediate characteristic of parylene chemistry in such a way that the molecule is prevented from participating in the nucleation and propagation reactions of polymerization.²⁴ Evaporated metals, metal salts, and organometallic complexes have all been found to prevent the deposition of the CVD polymers, but well-defined selectively grown CVD polymer features with lateral dimensions on the order of a few microns have only been realized with evaporated metals patterned on surfaces by photolithography.²⁴ In this report, we present several non-photolithographic methods that

can be used for fabrication of patterned parylene-based CVD polymer films. These methods use transition metal salts and evaporated transition metal layers in combination with μ CP to activate or deactivate regions of the surface to polymer growth. We have used this method to generate patterned CVD polymer films with features ranging from 1.5 to 35 μ m in width.

Experimental Section

The polymer CVD reaction system used in these studies has been described previously.²⁵ Parylene-N and parylene-C were prepared from [2.2]paracyclophane (Sigma-Aldrich) and dichloro-[2.2]paracyclophane (courtesy of Specialty Coating Systems) monomers, respectively, and α,α' -dichloro-*p*-xylene (Aldrich) was used for PPV deposition. All monomers were pyrolyzed at 675 °C and 0.05 Torr to form *p*-xylylene (which is the reactive monomer for polymerization) or a *p*-xylylene derivative.^{27,28} The films were deposited at 10 Å/s and 25 °C onto silicon(100) surfaces metallized with silver (400 Å thick deposited at 10 Å/s) or gold (50 Å chromium adhesion layer at 2 Å/s, followed by 200 Å thick gold layer deposited at 5 Å/s).

The processes used for generating the elastomeric stamp and depositing alkanethiols onto metal surfaces by μ CP have been discussed previously in detail.²⁹ The hexadecanethiol (HDT, CH₃(CH₂)₁₅SH) and 16-mercaptohexadecanoic acid (MHA, COOH-(CH₂)₁₅SH) inks were prepared as 1 mM solutions in 200 proof ethanol. Figure 1A shows a process for activation of regions of a gold or silver surface to polymer growth by deposition of a monolayer of HDT or MHA by μ CP. In this approach, the best results were obtained if the metal substrates were not rinsed with solvents prior to μ CP and polymer CVD. Alternatively, the monolayers formed by μ CP could be used in conjunction with iron salts to define regions of growth inhibition on the surface, as shown in Figures 1B and 1C. In this case, the carboxylic acid end group of the MHA monolayer is used to spatially control the

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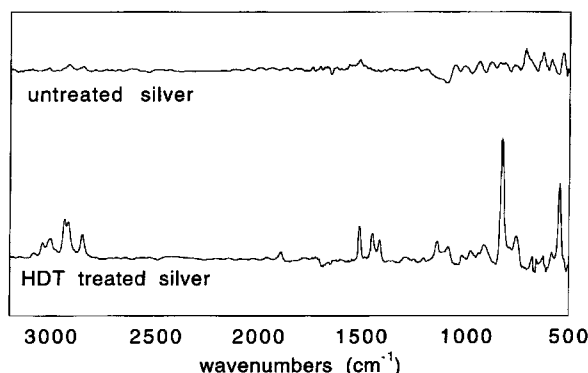


Figure 2. IRRAS spectra of a parylene-N film deposited on an untreated silver surface and an HDT-treated silver surface.

deposition of iron salts on the surface, which are known to inhibit CVD polymer growth. This approach is particularly flexible, since the MHA could be printed directly onto the surface with the stamp (Figure 1B), or deposited in the unprinted regions after μ CP an alkanethiol with an end group that does not interact with the iron salt, such as HDT (Figure 1C). In this way, both discrete polymer structures and discrete "holes" in a continuous polymer film could be fabricated using a stamp formed from a single master. Association of the iron salt with the carboxylic acid end group of MHA was performed by dipping the printed substrate into an aqueous iron sulfate or iron(III) chloride solution (0.2 mg/mL in deionized water) for 20 s and then running a stream of deionized water over the surface for 10 s.

The structure of the patterned CVD polymer films was analyzed with a Digital Nanoscope 3000 atomic force microscope (AFM) in tapping mode, and film thicknesses were measured with a P-10 profilometer with a tip radius of 2 μ m. Fourier transform infrared reflection-absorption spectroscopy (IRRAS) was performed with a Nicolet 800 spectrometer.

Results and Discussion

Influence of Alkanethiol Monolayers on CVD Polymer Film Deposition. Patterned alkanethiol self-assembled monolayers (SAMs) can be formed readily by μ CP on some of the metals shown previously to inhibit the growth of parylene-based CVD polymers, such as silver and gold.²⁴ These metals prevent polymer deposition by interacting with the *p*-xylylene reactive intermediate characteristic of parylene CVD chemistry in such a way that the initiation and propagation reactions of polymerization are quenched on the metal-treated surface. We have found that this quenching interaction does not occur if the metal has been covered with an alkanethiolate monolayer. Figure 2 shows IRRAS spectra, taken ex-situ, of two silver substrates run simultaneously in the deposition chamber during parylene-N CVD. Prior to polymer deposition, a monolayer of HDT was formed on one of the silver surfaces, while the other substrate was left untreated. The IRRAS spectra show that polymer deposition is inhibited on the untreated surface (as expected for these reaction conditions)²⁴ but does occur on the HDT-treated silver surface, with the spectral characteristics of the deposited polymer in good agreement with those reported in the literature for parylene-N. The same effect was observed on gold surfaces; i.e., no growth was observed on the untreated metal surface and polymer deposition on the surface derivatized with an HDT SAM. On surfaces treated with carboxylic acid-terminated MHA monolayers, polymer growth was similar to that on HDT-modified substrates. Therefore, covering the metal surface with an alkanethiolate monolayer allows polymer deposition by preventing the interaction between the metal and *p*-xylylene that would otherwise inhibit polymer growth.

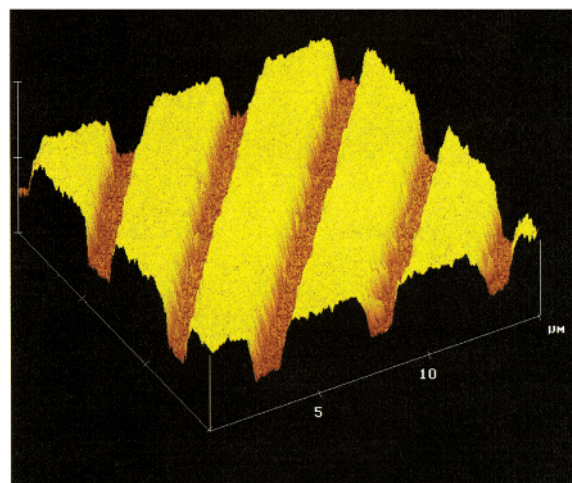
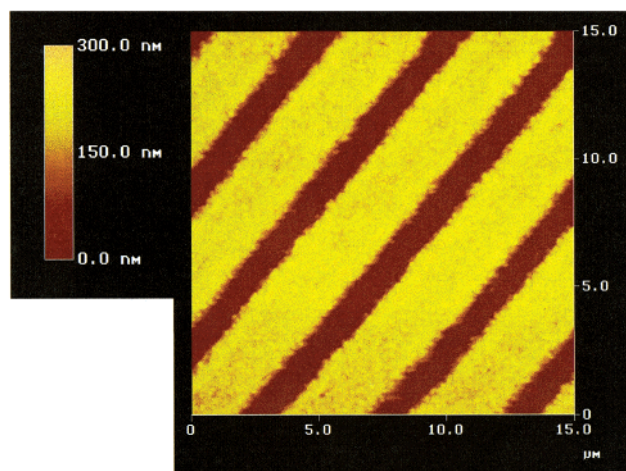


Figure 3. AFM images of parylene-C grown on μ CP silver surfaces (3 μ m line width).

This same trend is observed for parylene-C deposited by CVD, but not for CVD PPV, which is a reflection of the fact that silver and gold have been found to be more effective at preventing the deposition of parylenes on surfaces²⁴ than CVD PPV.²³

Fabrication of Patterned CVD Polymer Films Through μ CP of Alkanethiols. Deposition of micron-scaled patterns of alkanethiols on metal surfaces by μ CP presents a simple way to direct the formation of micron-sized polymer features. Figure 3 shows an AFM image of an array of parylene-C lines grown on a silver surface printed with MHA. The width and periodicity of the lines are 3 μ m, which are in good agreement with the features of the stamp used for μ CP. The overall thickness of the completely selectively grown film is 1500 Å. Fabrication of arrays of discrete, micron-sized features is also possible with the μ CP approach. Figure 4 shows an AFM image of parylene-N grown on a silver surface patterned with 1.5 μ m diameter HDT circles prior to polymer deposition. The resulting polymer layer consists of discrete, 2500 Å thick cylinders with the same diameter as that of the features of the PDMS stamp used for μ CP.

Effect of Metal Surface Selection on the Structure and Thickness of Selectively Grown CVD Polymers. For a given parylene-based CVD polymer chemistry and set of deposition conditions, the maximum attainable thickness of the selectively grown feature was solely a function of the metal used for μ CP. This thickness limit

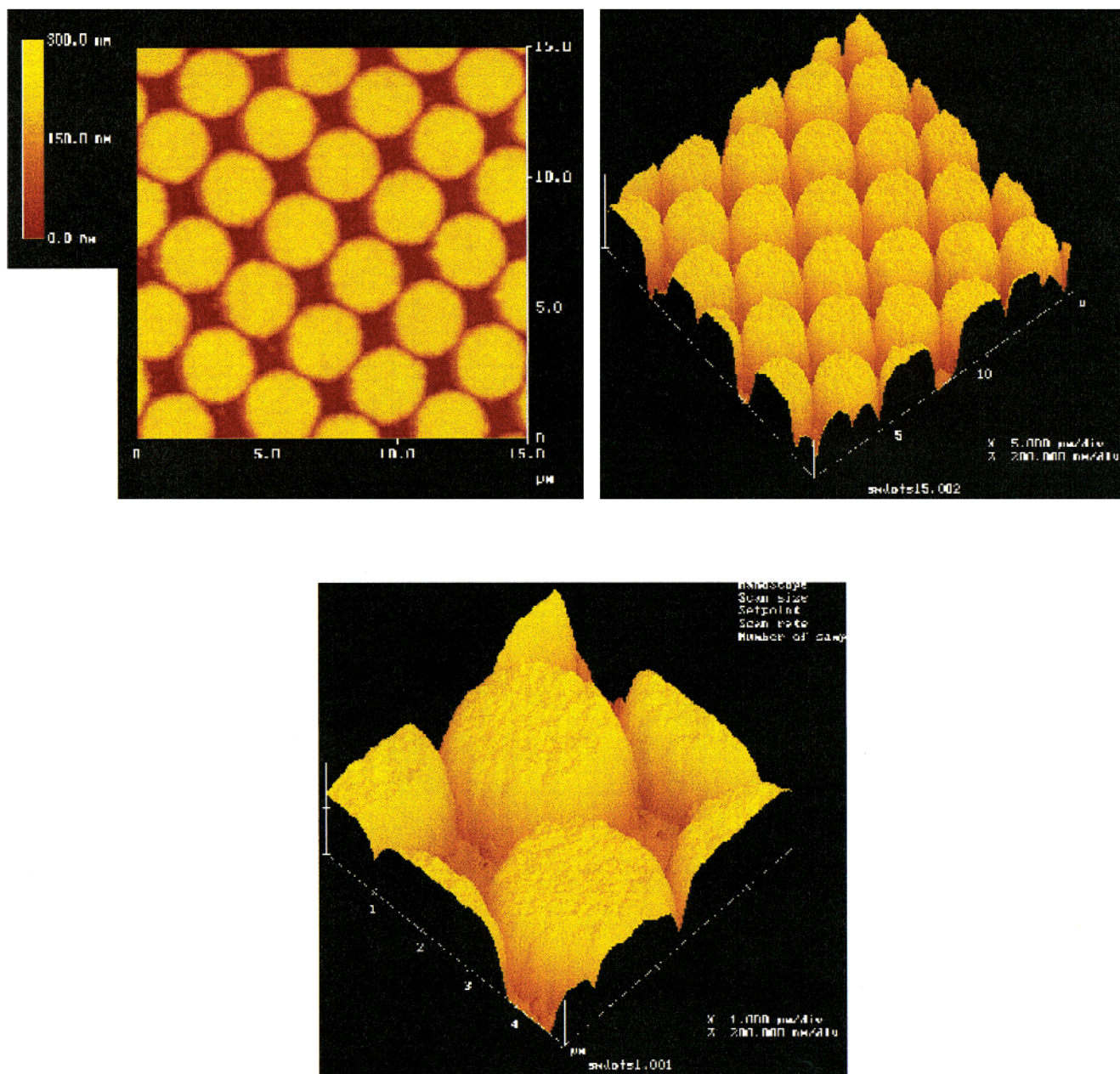


Figure 4. AFM images of parylene-N grown on μ CP silver surfaces (1.5 μ m diameter).

reflects the relative ability of each metal at preventing polymerization on the surface. Figure 5 shows profilometry scans of parylene-N, parylene-C, and PPV features grown by CVD on silver surfaces patterned as shown in Figure 1A using a stamp with circles (15 μ m diameter) and HDT as the ink. For comparison, also shown is a profilometry scan of features grown on gold surfaces patterned in the same manner and subjected to the same growth conditions. On all of the surfaces, polymer growth was allowed to proceed until deposition occurred on the unprinted portions of the metal. For the parylenes, thicker features are achieved on silver surfaces as compared to gold (6000 and 1500 Å on silver versus 1500 and 1000 Å on gold for parylene-N and parylene-C, respectively). For CVD PPV, little feature definition is detected on silver substrates, and only thin, poorly formed features are observed on gold. These trends in the maximum feature thickness generated on each metal surface are consistent with the relative activity of each metal in inhibiting polymer growth observed previously.²⁴ For all polymers and metal surfaces,

replacing HDT with MHA did not change the maximum thickness of the selectively grown features. This suggests that there is no significant difference in the effect each of these end groups (hydrocarbon for HDT and carboxylic acid for MHA) has on the nucleation and propagation processes of the CVD polymer.

Use of μ CP in Conjunction with Metal Salts for Selective Growth of CVD Polymers. One constraint of using alkanethiols deposited by μ CP to control CVD polymer nucleation and growth is that the technique is generally limited to silver and gold surfaces (although copper³⁰ can also be used if kept in an inert atmosphere prior to alkanethiol deposition³¹). We have demonstrated^{23,24} that other metals, such as iron and ruthenium, are more effective at inhibiting the deposition of polymer prepared with parylene-based CVD chemistry, especially

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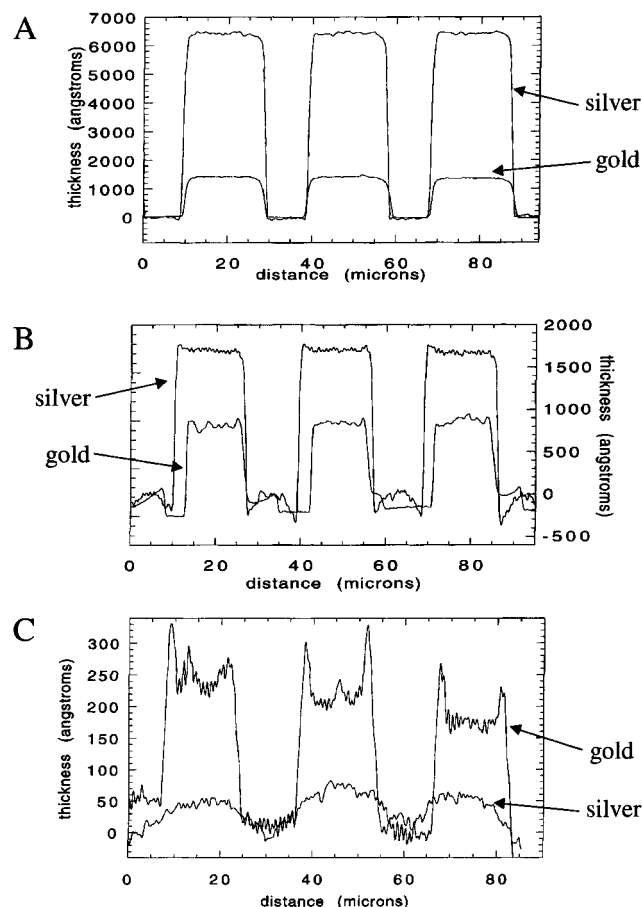


Figure 5. Profilometry of (A) parylene-N, (B) parylene-C, and (C) PPV growth on silver and gold surfaces that were patterned with HDT by μ CP prior to polymer deposition. (The spikes on the edges of the features formed on the gold surfaces are believed to be an artifact of the profilometry scan.)

CVD PPV. Although these metals can be deposited and patterned by electron-beam evaporation and conventional photolithography, it is not simple to pattern these metals with SAMs by μ CP. Salts of iron and ruthenium have also been shown to prevent polymer deposition on surfaces,²³ but it is not straightforward to deposit spatially complex patterns of salts on the substrate with conventional photolithography. However, μ CP presents a simple way to define metal salts deposited from solution in localized regions of a surface, since there is a large amount of flexibility in choosing the chemical functionality of the alkanethiol end group. In particular, μ CP of alkanethiols with carboxylic acid end groups such as MHA can control the areas of iron salt exposure on a surface (Figure 1B and C). During polymer deposition, growth only occurs in the iron-free regions of the substrate. This method is particularly suited for gold substrates, which have less activity in inhibiting parylene-based CVD polymer growth than silver or iron, and for CVD PPV, the deposition of which is not greatly inhibited by gold or silver.²³

Photoluminescence from a CVD PPV film prepared with the method outlined in Figure 1B is shown in Figure 6A. The film consists of an array of "holes" 35 μ m in diameter and periodicity in the polymer film, which is in good agreement with the geometry of the stamp used for μ CP. Figure 6B shows photoluminescence from a patterned PPV film generated as outlined in Figure 1C. Surface profilometry (shown in the inset) of the features shows fairly sharp edge definition, with lateral feature sizes 12.5 μ m

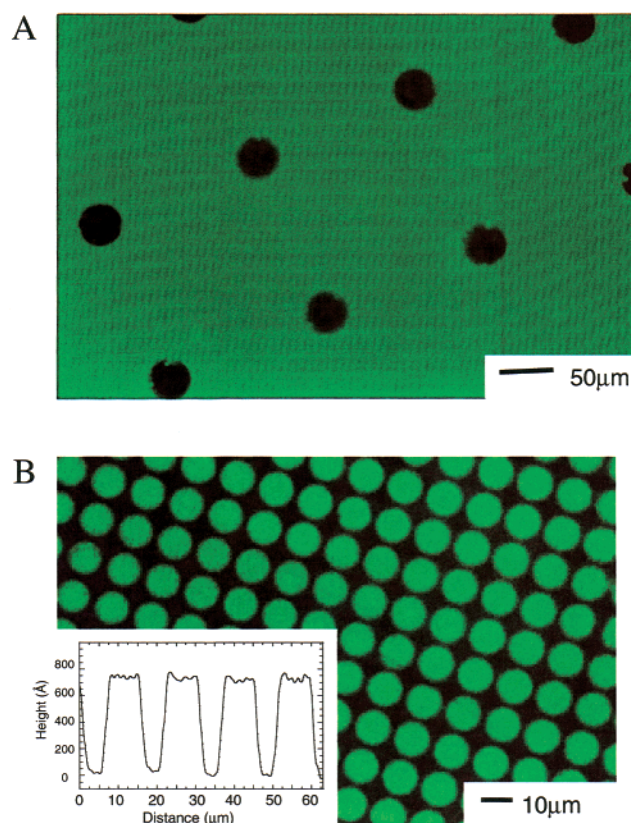


Figure 6. Photoluminescence from selectively grown CVD PPV films generated by combining μ CP alkanethiols and a growth-inhibiting iron salt: (A) holes in the PPV film (35 μ m in diameter) fabricated as shown in Figure 1B, using MHA in the printing step and iron(III) chloride as the growth-inhibiting salt; (B) an array of CVD PPV dots (12.5 μ m in diameter separated by 2.5 μ m) fabricated as shown in Figure 1C, using HDT in the printing step, MHA in the unprinted regions, and iron(II) sulfate as the growth-inhibiting salt.

in diameter separated by 2.5 μ m, and a film thickness of 750 Å. These dimensions are representative of those required for display applications.

Conclusions

Use of alkanethiols in conjunction with transition-metal inhibitors offers a flexible method for creating patterned vapor-deposited polymer films of interest in electronics and optoelectronics. The technique has advantages over other patterning methods in that it is parallel in nature, does not require that the polymer layer be exposed to solvents, and generates micron-sized features with good edge definition. In addition, since the polymer deposits onto the substrate in the desired pattern, there is no need for further processing steps that could have an adverse effect on characteristics such as luminescence or surface roughness. Since feature sizes relevant for use in light-emitting polymer-based displays and lower-speed integrated circuits are easily realized with this approach, it may offer a fast, low-cost way for integrating these materials into devices.

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