A Directly Patternable, Click-Active Polymer Film via Initiated Chemical Vapor Deposition

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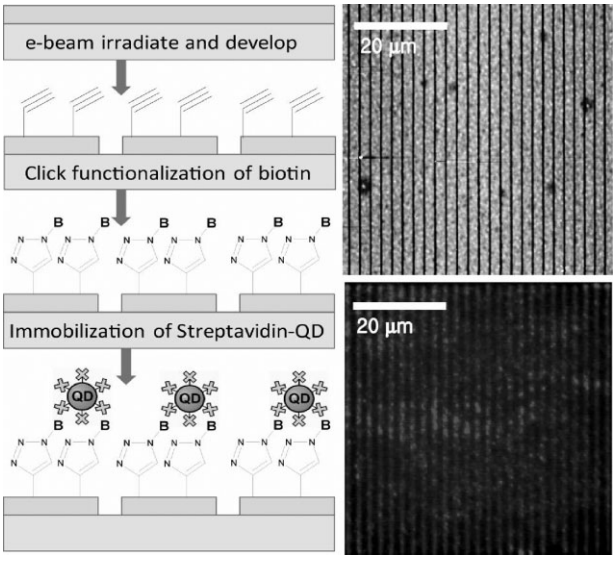
Click-active surfaces patterned at 200 nm resolution are demonstrated using the dual functional polymeric film, poly(propargyl methacrylate) (PPMA). The commercially available monomer of propargyl methacrylate (PMA) is polymerized in a single step by initiated chemical vapor deposition (iCVD). FT-IR and X-ray photoelectron spectroscopy confirm retention of the click-active acetylene functional group in the bulk and surface of the iCVD film, respectively. Treating substrates with silane coupling agents prior to deposition results in grafting of iCVD PPMA polymers onto various inorganic surfaces. This grafting technique provides the chemical and mechanical stability required for the PPMA layer to survive the subsequent wet chemical steps used for click functionalization. Successful attachment of an azido-functionalized coumarin dye is demonstrated. Moreover, the PPMA film displays direct positive-tone sensitivity to e-beam irradiation, which enables e-beam patterning without the use of a resist layer. Direct e-beam exposure of the multifunctional PPMA iCVD layer results in a 200 nm pattern to which quantum dot nanoparticles are selectively conjugated on the substrates by click chemistry.



Introduction

Nanopatterned functional surfaces are excellent vehicles for exploring the interfacial interactions of biological components and can be utilized for applications that include controlled drug release, biosensors, and artificial skin.[1–3] The desire for immobilization onto specific surface sites with high adhesion and high selectivity has motivated widespread interest in 'click' chemistry, which quickly and selectively creates covalent linkages. One of the most efficient and versatile click reactions is the Huisgen 1,3-dipolar cycloaddition[4] in which the reaction of azides and terminal alkyne groups are catalyzed by Cu^{I}. These Sharpless-type click reactions display fast reaction rates, are highly regioselective, and can be performed in various solvents, including water at biologically relevant temperatures (25–70 °C).[5]

The high reactivity of the desired azide or alkyne groups presents challenges for both the synthesis and patterning

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Macromol. Rapid Commun. **2008**, *29*, 1648–1654

DOI: 10.1002/marc.200800404

of click active surfaces. Multistep syntheses have been successful, for example, a self-assembled monolayer initially formed with bromo-terminal groups was subsequently converted into the azido-terminated functionality.[6] Alternatively, non-commercially available monomers have been synthesized for subsequent polymerization. For example, alkyne-functionalized paracyclophane monomers were synthesized and subsequently polymerized by a chemical vapor deposition (CVD) process to obtain a clickable surface.[7] Similarly, an azido-functionalized methacrylate was synthesized for use in an atom transfer radical polymerization.[8]

The direct patterning of clickable surfaces is also challenging because of the high reactivity of clickable functionalities. For example, azides can be easily photolyzed with ultraviolet light (UV).[9] The undesirable attack of the alkyne functionality by the radicals generated in the course of polymerization also leads to highly branched and cross-linked polymers.[8] For these reasons, clickable surfaces have been difficult to pattern by traditional subtractive lithographic approaches. Instead additive approaches have been employed, for example, the microcontact printing of alkynes was applied on an azide surface to form a 5 μm stripe pattern.[6,7] Alternatively, electrochemical activation of a Cu^{I} catalyst was selectively applied on a Au electrode with azide self-assembled monolayers (SAMs) with the separation of 10 μm between the two electrodes.[10]

The synthesis of a click active surface that can be directly patterned by irradiation would enable traditional lithography to be employed for the creation of higher resolution patterns. In this report, poly(propargyl methacrylate) (PPMA) films were successfully synthesized by initiated CVD (iCVD) in one-step from commercially available monomer. The mild temperatures of the iCVD process permit retention of delicate alkyne functional groups.[11] Feature sizes of 200 nm were achieved by direct electron beam (e-beam) lithography. As the PPMA itself is sensitive to e-beam exposure, the need for a conventional resist layer is avoided. Grafting of the iCVD PPMA layer to the substrate was achieved in order to obtain mechanical and chemical stability of polymer films for this nanometer-scale resolution. Click chemistry employing the pendant alkyne of the PPMA was demonstrated before and after patterning. Thus, iCVD PPMA exhibits the dual functions of 'clickability' and direct e-beam 'patternability' at a nanometer scale.

Experimental Part

iCVD

The procedure of the iCVD process is described in detail elsewhere.[12] Propargyl methacrylate (PMA, Alfa Aesar, 98%) and *tert*-butyl peroxide (Aldrich, 98%) were purchased and used without further purification. PMA and initiator were vaporized at room temperature and introduced into the iCVD chamber at a flow rate of approximately 4 and 1.5 sccm, respectively. The flow rates were controlled with mass flow controllers (MKS 1490A, MKS 1152C). The polymerization reaction was initiated with the filament at 280 °C. The process pressure was 800 mTorr controlled by a PID controllable butterfly valve (MKS 248 flow control valve). Film thicknesses were monitored in situ by interferometry; approximately 200 nm of the PPMA film was deposited in 20 min.

Plasma Polymerization

A plasma polymerized PPMA film was obtained in a parallel plate chamber with 150 mm diameter electrodes. The process pressure was 100 mTorr, and PMA was introduced at a flow rate of 5 sccm. An amount of 5 W of a 13.56 MHz power source was applied with continuous RF discharge. After 10 min, the plasma polymerized PPMA film was obtained with a thickness of 100 nm.

Surface Grafting

Trichlorovinyl silane (TCVS, 0.5 mL, from Aldrich, 97%) was placed in a dessicator. An oxygen-plasma-treated Si wafer was exposed to TCVS vapor at 25 °C for less than 5 min. The process pressure in the dessicator was 100 mTorr. Exactly the same iCVD conditions were applied to the silane-treated Si wafer for grafted PPMA on Si wafer.

Click Chemistry

7-Methoxycoumarin-3-carbonyl azide (N_3-Coumarin, 4.0×10^{-3} M, AnaSpec Inc., 97%), copper(II) sulfate (1.0×10^{-3} M), and sodium ascorbate (2.0×10^{-3} M) were solubilized in 10 mL of *N*,*N*-dimethylformamide (DMF). A piece of grafted PPMA film (100 nm thick) on Si wafer was placed into the solution and stirred by a magnetic bar at 25 °C for 16 h. After the reaction, the sample was rinsed with DMF several times and dried with nitrogen purge. Ten minutes of ultrasonication was applied to the N_3-coumarin-functionalized PPMA film to remove physically adsorbed, unreacted reaction residue. Maintaining the same reaction conditions of N_3-coumarin except for replacing the N_3-coumarin with azido-biotin (Aldrich Inc.) resulted in a biotin-functionalized PPMA surface. The quantum dot (QD) conjugation was achieved by soaking biotin-functionalized substrates in 1.0×10^{-3} M of streptavidin-derivatized QD particles (Qdot 605 streptavidin conjugate, Invitrogen) in water for 30 min. Afterwards, the physically attached QDs were rinsed with excessive water and ultrasonicated for 10 min.

Photolithography

OCG 825 was used as the photoresist. After spin-coating to form a 1 μm thick film, it was soft-baked at 90 °C. The film was exposed to UV light with the photomask and developed with OCG 934, as the developer. On top of the patterned photoresist layer, PPMA was

deposited by the iCVD technique and the PPMA film on the photoresist pattern was lifted off by ultrasonication for 5 min in acetone.

e-Beam Lithography

The e-beam was directly irradiated on top of the iCVD PPMA films, and negative tone patterning was obtained at a dose of 50 mC · cm^{-2}. Developing for 90 s with DMF completed the 200 nm feature size of the PPMA pattern.

Characterization

FT-IR spectra were obtained using a Nexus 870 (Thermo Electron Corporation). X-ray photoelectron spectroscopy (XPS) was carried out on a Kratos Axis Ultra spectrometer equipped with a monochromatized Al K_α source. The measured XPS spectra were non-linear square fitted for quantitative analyses. The e-beam pattern was examined by optical microscopy (Olympus, Model CX41) with a maximum magnification of 1 000. Fluorescence images were gathered using an AxioSkop 2 MAT, Zeiss with an excitation wavelength of 365 nm for N_3-coumarin and 605 nm for red CdSe/ZnS QDs. Atomic force microscopy (AFM) images were obtained using a DI3100, Digital Instruments.

Results and Discussion

Preparation and Characterization of Click-Active iCVD PPMA Film

Figure 1a and b represent the FT-IR spectra of PMA monomer and iCVD PPMA, respectively. Both spectra display the characteristic bands for alkynes: a C–H stretch peak around 3 200 cm^{-1} and a C≡C stretch peak around 2 100 cm^{-1}.[13] The nearly identical intensity of the two FT-IR peaks distinctly indicates the retention of the pendant click-active alkyne functionalities during the iCVD polymerization process. In contrast, the film that results from plasma polymerization of PMA contains virtually no characteristic alkyne peaks in the FT-IR spectra, which demonstrates that the alkynes are completely destroyed by the applied plasma (Figure 1c). Instead, the increase of the sp^3 C–H peak intensity around 3 000 cm^{-1} in Figure 1c infers that the decomposed alkynes are converted into click-inert alkyl groups. The contrast between Figure 1b and c clearly displays the non-destructive characteristics of the iCVD process relative to plasma polymerization. The C=C stretch peak around 1 600 cm^{-1} observed for the PMA monomer (Figure 1a) disappears in iCVD PPMA (Figure 1b), which indicates that the PMA monomer fed into the chamber is converted into a PPMA polymer film on the Si wafer by the iCVD vinyl polymerization process.[14] The increase of the sp^3 C–H peak intensity around 3 000 cm^{-1} in Figure 1b also supports the radical polymerization of PMA by the iCVD process.

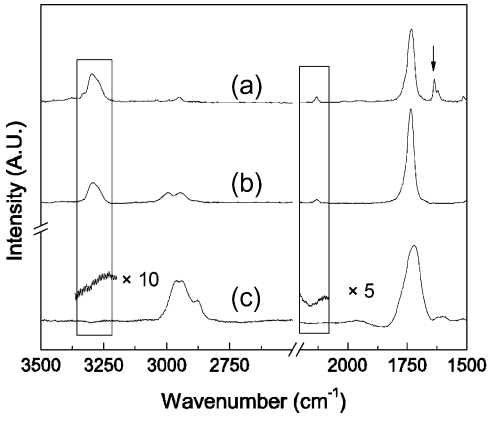

Figure 1. FT-IR spectra of a) PMA monomer, b) iCVD PPMA, and c) plasma-polymerized PPMA. Rectangular regions represent the C–H stretch peak in the alkyne group (around 3 200 cm^{-1}) and the C≡C stretch peak in the alkyne group (around 2 100 cm^{-1}). The arrow denotes the C=C stretch peak in the monomer (a) (around 1 600 cm^{-1}) which, due to vinyl polymerization, is absent is the iCVD film (b). The iCVD film (b) clearly retains the clickable alkyne group while this functionality is destroyed by plasma polymerization (c).

Chemical and mechanical stability in solvents is essential because the subsequent click functionalization and patterning processes consist of a series of wet chemical steps. For this purpose, PPMA film was covalently grafted onto the Si wafer surface by using pre-treatment of a vinyl-containing silane coupling agent, TCVS, and subsequent iCVD process to achieve solvent resistance of the polymer layer.[15] Ultrasonication and tape tests demonstrated the greatly enhanced adhesion of iCVD PPMA grafted on to the Si surfaces (data not shown).[15] The surface-grafted PPMA was not soluble in common organic solvents such as tetrahydrofuran (THF), DMF, and acetone. No distinctive change was observed in the FT-IR spectra between before and after the solvent exposure.

The XPS spectra of the iCVD PPMA are shown in Figure 2 (also in Figure 3a). As expected, the XPS survey scan (Figure 3a, bottom) reveals only oxygen and carbon in a ratio of 23: 77, which corresponds very well to the theoretical O/C ratio of 2: 7. The C 1s high-resolution scan spectrum (Figure 2a) was non-linear least squares fitted using four Gaussian peaks, which provides a quantitative analysis that also matched with the known chemical structure of PPMA.[16] The calculated ratio of each carbon (C1/C2/C3/C4) was 57.5: 14.1: 14.3: 14.2, which is also close to the theoretical ratio of 4: 1: 1: 1. Of particular interest for a 'clickable' surface, is the intense peak at 284.8 eV, which corresponds to the carbons in the propargyl group and α-methyl methylene backbone. Thus XPS confirms that the alkyne groups identified in the bulk iCVD PPMA film by FT-IR are also present at the surface where their reactivity is desired. The O 1s high-resolution scan spectrum can also be

Macromol. Rapid Commun. **2008**, *29*, 1648–1654

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DOI: 10.1002/marc.200800404

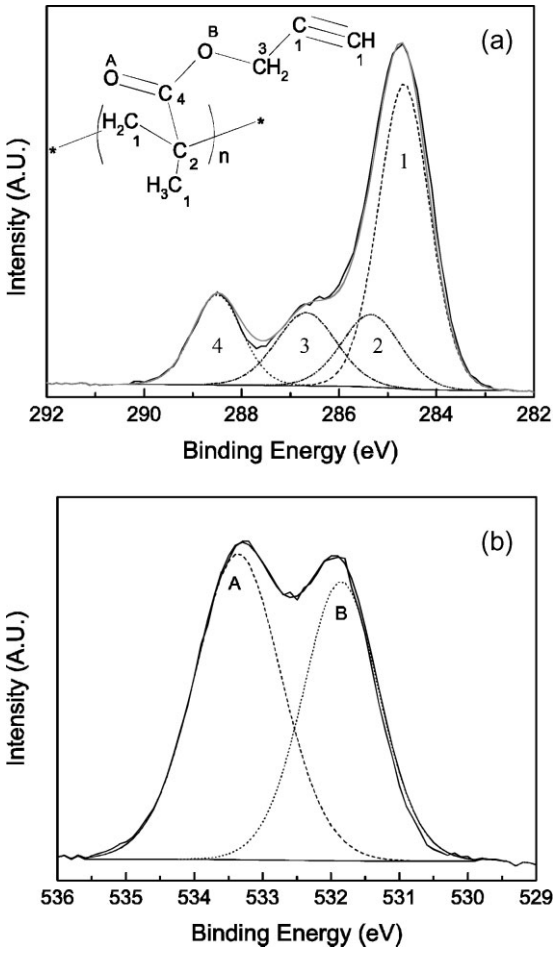


Figure 2. XPS high-resolution spectra of PPMA; a) C 1s and b) O 1s, respectively. The chemical structure is labeled with numbers, providing the assignment for (a), and capital letters, which correspond to the assignment for (b).

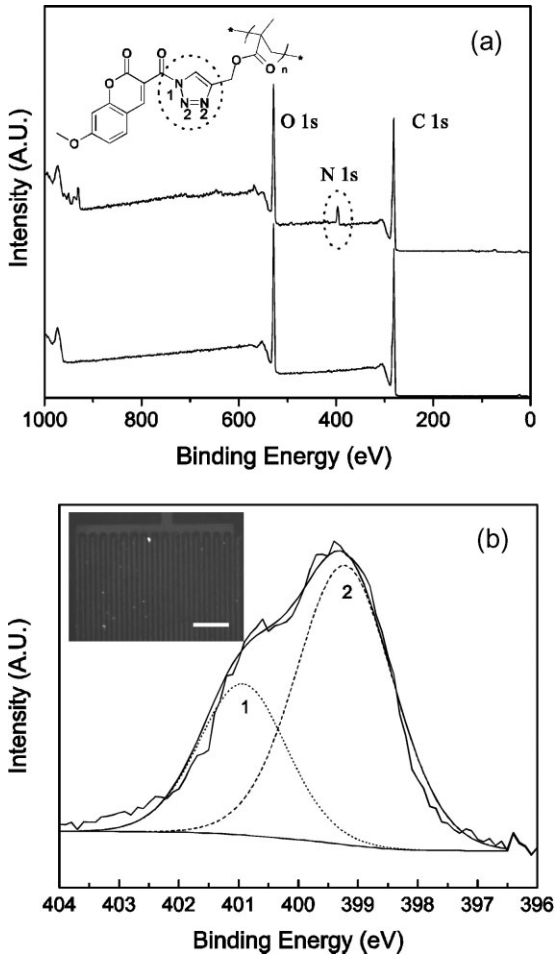
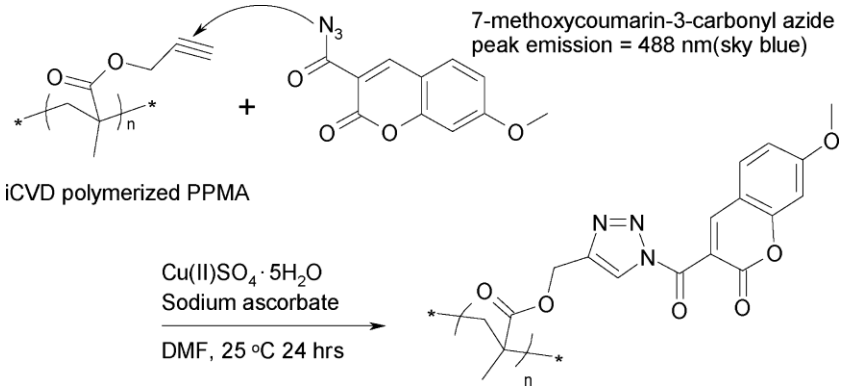


Figure 3. XPS: a) Survey scan of PPMA (bottom) and N_3-coumarin-functionalized PPMA films (top) and b) high-resolution N 1s scan data of N_3-coumarin-functionalized PPMA films by a click reaction, respectively. Dotted circles in (a) highlight the newly formed N 1s peak by the click reaction. The inset in (b) represents a fluorescence microscope image of a patterned PPMA film click-functionalized with N_3-coumarin. Scale bar in the inset represents 20 μm. Each superscripted number in the chemical formula of the click-functionalized PPMA in (a) corresponds to peaks assigned in the XPS N 1s spectrum in (b).

non-linear least squares fit to two independent peaks, which correspond to the two distinct oxygen sites in the acrylate group. The calculated ratio was 52:48, which closely matches the theoretical ratio of 1: 1. Therefore, the XPS analysis distinctly displays that the surface composition of the iCVD PPMA film is fully consistent with the expected molecular structure of PPMA. Moreover, these XPS results corroborate the FT-IR results and support the hypothesis that most of the reactive alkyne functionality survived during the iCVD polymerization reaction.

Click Chemistry on iCVD PPMA Film Surfaces

Onto the iCVD alkyne surface, click functionalization was applied by introducing azide conjugates. Click reactivity of the PPMA surface was assessed using XPS and fluorescence microscopy following attachment of a fluorescent dye. For this later purpose, an azido-derivatized blue fluorescent dye, N_3-coumarin ($\lambda_{em} = 488$ nm) was chosen as a conjugate. The Huisgen 1,3-dipolar cycloaddition between N_3-coumarin and iCVD PPMA was performed with copper(II) sulfate and sodium ascorbate in DMF solvent. Sodium ascorbate reduces copper(II) sulfate in situ to yield Cu^I ions that catalyze the cycloaddition reaction to form a triazole linkage between iCVD PPMA and N_3-coumarin (Scheme 1). After the reaction, repeated rinsing and ultrasonication were applied to eliminate all physisorbed species during the functionalization step. The grafting of iCVD PPMA to the substrate turned out to be a critical step to prevent the iCVD layer from delaminating during click functionalization, which enables the use of various organic solvents and purification with ultrasonication. XPS was applied to the iCVD PPMA film before and



Scheme 1. Click reaction between the iCVD PPMA film and an azido-functionalized fluorescent dye, N_3-coumarin.

after N_3-coumarin functionalization. A new indicative nitrogen peak around 400 eV was detected in the N_3-coumarin-functionalized iCVD PPMA surface in the survey scan spectrum, which was absent in freshly prepared iCVD PPMA (Figure 3a). Since the PPMA film does not contain any nitrogen-containing groups as previously demonstrated in Figure 2, the nitrogen groups at the polymer surface originated from the triazole group formed by the click reaction. Therefore, the appearance of a new nitrogen peak indicates that the cycloaddition of N_3-coumarin was successfully achieved. The N 1s high-resolution scan XPS spectrum also confirms the attachment of N_3-coumarin to the iCVD PPMA surface by click chemistry (Figure 3b). The nitrogen peaks were non-linear least squares fitted to two peaks, which were assigned as the amide bond in triazole (1 in Figure 3a) at 400.8 eV and two N=N bonds in triazole (2 in Figure 3a) at 399.2 eV.[16] The ratio of peak areas was calculated as approximately 1: 2, which is consistent with the chemical structure of N_3-coumarin-functionalized PPMA.[17]

The chemical selectivity of the click reaction with iCVD PPMA was assessed by applying a clickable fluorescent dye onto pre-patterned PPMA. To pattern PPMA, a conventional patterning process of photolithography was applied to PPMA.[16] To minimize the potential damage to the alkyne functionality in the PPMA film during the photolithography process, only a photoresist (PR) layer was pre-patterned first. Subsequently, iCVD PPMA was grafted onto the PR-patterned Si wafer. The lift-off of the patterned PR with acetone completes the patterning of the PPMA flim. The covalently grafted PPMA film was mechanically and chemically strong enough to enable an acetone-based lift-off process without damaging the click-active alkyne functionality. A well-defined 2 μm size line pattern was easily obtained according to the patterned PR film. The same click chemistry was applied onto this patterned PPMA surface, and a fluorescence microscope image (inset in Figure 3b) shows a sharp contrast of fluorescence from the blue N_3-coumarin dye. The fluorescence image was precisely aligned with the PPMA pattern. No fluorescence image degradation was observed after 10 min of ultrasonication, which confirms that the fluorescent dye on the PPMA film is covalently bound rather than just physically adsorbed.

Click Chemistry on e-Beam Patterned iCVD PPMA Film Surfaces

In addition to being able to undergo click reactions, the PPMA film itself is also e-beam sensitive. This unique multifunctional nature of the iCVD PPMA films is demonstrated by patterning them directly with e-beam lithography. Indeed a well-defined pattern on a nanometer scale was readily obtained with e-beam irradiation directly onto the iCVD PPMA film. The AFM image (Figure 4b) shows that the e-beam irradiated area was developed out with DMF for 90–120 s, and 200 nm stripe patterns were obtained with a dosage of 50 $mC \cdot cm^{-2}$ at 50 keV acceleration voltage. The e-beam sensitivity of PPMA allows an easy fabrication of a nanometer-sized pattern without the use of an additional e-beam resist, which substantially simplifies the whole patterning process (Figure 4a–ii) compared with a standard e-beam lithography procedure (Figure 4a–i). Moreover, the direct patterning process can also remove the potential of damaging the clickable alkyne groups on the e-beam resist through such processes as thermal annealing, exposure to organic solvents for the e-beam resist in spin coating, and resist removal. In addition, the developer for the direct e-beam patterning, DMF, is also widely used as an organic solvent for click chemistry so does not destroy the patterned PPMA surface any further. Therefore, if DMF is chosen as a solvent for the click reaction of e-beam-patterned PPMA, the development process can also be directly included in the click reaction step, so that the development and click reaction may occur simultaneously and the patterning-functionalization process can be further simplified.

The e-beam sensitivity of the PPMA film is attributable to the methacrylate backbone of PPMA. It is well known that a variety of methacrylate polymers such as poly(methyl methacrylate) (PMMA), poly(2-hydroxyethyl methacrylate), and poly(methyl methacrylic acid) are known to retain e-beam patternability.[18–20] Previously, negative-tone e-beam patterning of iCVD poly(glycidyl methacylate) films was also reported.[19] As one of the methacrylate polymers, iCVD PPMA also displayed e-beam sensitivity. However, compared with one of the standard e-beam resists like PMMA, PPMA requires about 10–50 times

Macromol. Rapid Commun. **2008**, *29*, 1648–1654

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DOI: 10.1002/marc.200800404

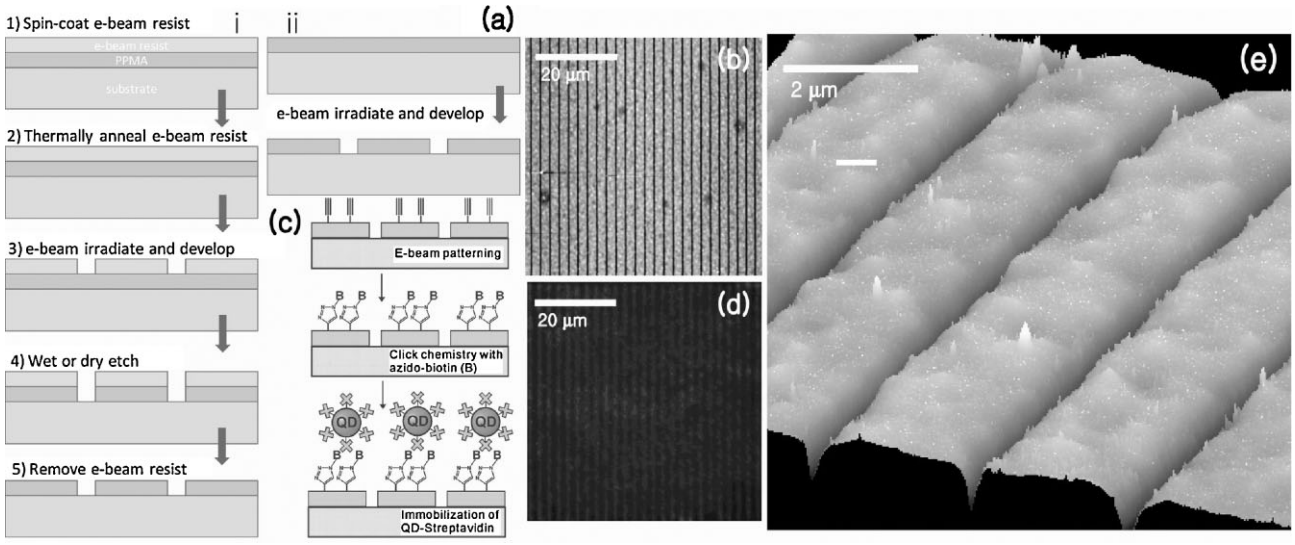

Figure 4. a) Schematic procedure of the standard e-beam lithography patterning (i) and direct e-beam patterning with e-beam sensitive PPMA film (ii) and b) AFM image of e-beam patterned iCVD PPMA. c) Schematic procedure of QD-streptavidin immobilization onto the patterned polymer film by biotin-streptavidin binding by click reaction. d) fluorescence microscope image and e) enlarged 3D AFM image of a e-beam patterned PPMA film conjugated with QD particles by click chemistry, respectively.

higher e-beam dose for the same level of pattern resolution. We suspect that during e-beam exposure some of the alkyne groups in PPMA cross-link simultaneously with the depolymerization of the methacrylate group. Hence, a higher dose of e-beam is required as compared with the acrylate resist with an inert methyl side group.

On top of the 200 nm line patterned iCVD PPMA surface formed using e-beam lithography, larger CdSe/ZnS QD nanoparticles ($\lambda_{em} = 605$ nm, $d = 15$ nm) were used to assess the pattern fidelity in click functionalization. First of all, azido-derivatized biotin was conjugated on pre-patterned iCVD PPMA substrates by a click reaction. Afterwards, streptavidin-functionalized QD particles were spread onto the biotin-functionalized PPMA film and strong biotin-streptavidin binding was successfully achieved in 30 min (Figure 4c). After the QD conjugation, a 10 min ultrasonication was applied to remove any physically adsorbed QDs and other unreacted residues. The click functionalization of the e-beam-patterned PPMA film could be clearly observed by using fluorescence microscopy and AFM (Figure 4d and 4e). The fluorescence from click-functionalized QDs is overlapped exactly with the pre-patterned e-beam pattern of the PPMA film (Figure 4d). Similarly, the surface of the unexposed area from e-beam irradiation shows a high surface density of QDs, which appear shown as white dots in the AFM image (Figure 4e). On the other hand, a negligible amount of QD particles was observed on the etched out area. This obvious contrast in QD particle density on the surface is totally consistent with the fluorescence microscope image. Similar to the preceding observation, the mechanical and chemical stability gifted by the grafting agent again ensures the reliable e-beam patterning and click reaction of the iCVD PPMA. The dual functionality of clickability and e-beam sensitivity in the iCVD PPMA can offer a powerful tool for various selective surface modification applications.

Conclusion

In conclusion, a new rapid synthetic pathway for depositing the click-active polymer coating of PPMA was obtained by a simple one-step iCVD process from a commercially available monomer, PMA. The pendent alkyne groups in PPMA were clearly observed in FT-IR and XPS spectra. By introducing a surface grafting agent to the iCVD process, the chemical and mechanical stability of the iCVD clickable layer was greatly enhanced. The well-defined alkyne surface functionality enables click chemistry through selective reactivity with azides. Furthermore, the PPMA film also demonstrated sensitivity to e-beam irradiation, which enabled clickable substrates that have nanometer-scale patterns. Direct e-beam exposure of this multifunctional iCVD layer gave rise to a 200 nm pattern, and QD particles were selectively conjugated on the substrates by click chemistry. Because the iCVD layer itself is e-beam sensitive, no additional resist layer was required. Combined with the advantages of the CVD process, such as a conformal coverage, non-sensitivity to the substrates, and ability to be grafted on various substrates,[11] the

clickable iCVD polymer e-beam sensitive layer can be a design platform for immobilized bio-devices including biosensors, bio-assays, drug discovery, bio-micro-electro-mechanical systems (bio-MEMS), microfluidic devices, and tissue engineering.[1]

Acknowledgements: This research was supported by the *U.S. Army* through the Institute for Soldier Nanotechnologies, under Contract DAAD-19-02-D-0002 with the U.S. Army Research Office. This work made use of *MIT*'s shared scanning-electron-beam-lithography facility in the Research Laboratory of Electronics.

Received: July 1, 2008; Accepted: August 11, 2008; DOI: 10.1002/marc.200800404

Keywords: chemical vapor deposition; click chemistry; e-beam lithography; fluorescence; surface chemistry; surface patterning; surfaces

[1] R. S. Kane, S. Takayama, E. Ostuni, D. E. Ingber, G. M. Whitesides, *Biomaterials* **1999**, *20*, 2363.
[2] D. Falconnet, G. Csucs, H. M. Grandin, M. Textor, *Biomaterials* **2006**, *27*, 3044.
[3] W. Senaratne, L. Andruzzi, C. K. Ober, *Biomacromolecules* **2005**, *6*, 2427.
[4] H. C. Kolb, M. G. Finn, K. B. Sharpless, *Angew. Chem. Int. Ed.* **2001**, *40*, 2004.
[5] J. F. Lutz, *Angew. Chem. Int. Ed.* **2007**, *46*, 1018.
[6] D. I. Rozkiewicz, D. Janczewski, W. Verboom, B. J. Ravoo, D. N. Reinhoudt, *Angew. Chem. Int. Ed.* **2006**, *45*, 5292.
[7] H. Nandivada, H. Y. Chen, L. Bondarenko, J. Lahann, *Angew. Chem. Int. Ed.* **2006**, *45*, 3360.
[8] B. S. Sumerlin, N. V. Tsarevsky, G. Louche, R. Y. Lee, K. Matyjaszewski, *Macromolecules* **2005**, *38*, 7540.
[9] R. S. Pandurangi, P. Lusiak, R. R. Kuntz, W. A. Volkert, J. Rogowski, M. S. Platz, *J. Org. Chem.* **1998**, *63*, 9019.
[10] N. K. Devaraj, P. H. Dinolfo, C. E. D. Chidsey, J. P. Collman, *J. Am. Chem. Soc.* **2006**, *128*, 1794.
[11] W. T. Tenhaeff, K. K. Gleason, *Adv. Funct. Mater.* **2008**, *18*, 969.
[12] K. Chan, K. K. Gleason, *Langmuir* **2005**, *21*, 8930.
[13] D. Lin-Vien, "*The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*", Academic Press, Boston 1991.
[14] W. S. O'Shaughnessy, M. L. Gao, K. K. Gleason, *Langmuir* **2006**, *22*, 7021.
[15] S. G. Im, P. J. Yoo, P. T. Hammond, K. K. Gleason, *Adv. Mater.* **2007**, *19*, 2863.
[16] J. F. Moulder, W. F. Stckle, P. E. Sobol, K. D. Bomben, "*Handbook of X-ray Photoelectron Spectroscopy*", Eden Prairie, MN 1995.
[17] R. D. Rohde, H. D. Agnew, W. S. Yeo, R. C. Bailey, J. R. Heath, *J. Am. Chem. Soc.* **2006**, *128*, 9518.
[18] J. N. Helbert, "*Handbook of VLSI microlithography: Principles, Technology, and Applications*", Noyes Publications, Park Ridge, N.J. 2001.
[19] Y. Mao, N. M. Felix, P. T. Nguyen, C. K. Ober, K. K. Gleason, *J. Vac. Sci. Technol. B* **2004**, *22*, 2473.
[20] Y. Mao, K. K. Gleason, *Macromolecules* **2006**, *39*, 3895.

DOI: 10.1002/marc.200800404