[4] S. E. Shaheen, C. J. Brabec, N. S. Sariciftci, F. Padinger, T. Fromherz, J. C. Hummelen, *Appl. Phys. Lett.* **2001**, *78*, 841.
[5] P. Schilinsky, C. Waldauf, C. J. Brabec, *Appl. Phys. Lett.* **2002**, *81*, 3885.
[6] M. M. Wienk, J. M. Kroon, W. J. H. Verhees, J. Knol, J. C. Hummelen, P. A. van Hal, R. A. J. Janssen, *Angew. Chem. Int. Ed.* **2003**, *42*, 3371.
[7] W. U. Huynh, J. J. Dittmer, A. P. Alivisatos, *Science* **2002**, *295*, 2425.
[8] B. Sun, E. Marx, N. C. Greenham, *Nano Lett.* **2003**, *3*, 961.
[9] B. Schweitzer, H. Bässler, *Synth. Met.* **2000**, *109*, 1.
[10] B. O'Regan, M. Grätzel, *Nature* **1991**, *353*, 737.
[11] A. Hagfeldt, M. Grätzel, *Acc. Chem. Res.* **2000**, *33*, 269.
[12] A. L. Roest, J. J. Kelly, D. Vanmaekelbergh, E. A. Meulenkamp, *Phys. Rev. Lett.* **2002**, *89*, 036 801/1.
[13] C. Pacholski, A. Kornowski, H. Weller, *Angew. Chem. Int. Ed.* **2002**, *41*, 1188.
[14] H. C. F. Martens, P. W. M. Blom, H. F. M. Schoo, *Phys. Rev. B* **2000**, *61*, 7489.
[15] I. H. Campbell, T. W. Hagler, D. L. Smith, J. P. Ferraris, *Phys. Rev. Lett.* **1996**, *76*, 1900.
[16] A. Hagfeldt, M. Grätzel, *Chem. Rev.* **1995**, *95*, 49.
[17] The intensity was determined by comparing the measured J_{SC} with the J_{SC} at 1 sun intensity, which was obtained from the convolution of the spectral response with the solar AM1.5 spectrum, and correcting for the small nonlinearity of the light intensity dependence using $I = I(1\ \text{sun}) \times [J_{SC}/J_{SC}(1\ \text{sun})]^{1/n}$) with $n = 0.93$.
[18] X. Wei, Z. V. Vardeny, N. S. Sariciftci, A. J. Heeger, *Phys. Rev. B* **1996**, *53*, 2187.
[19] M. Shim, P. Guyot-Sionnest, *J. Am. Chem. Soc.* **2001**, *123*, 11 651.
[20] T. J. Savenije, J. M. Warman, A. Goossens, *Chem. Phys. Lett.* **1998**, *287*, 148.

Dip-Pen Nanolithography of Chemical Templates on Silicon Oxide**

By *Steven E. Kooi*, *Lane A. Baker*, *Paul E. Sheehan*, and *Lloyd J. Whitman**

In the search for new methods to pattern materials on the nanoscale, DPN[1] has emerged as a flexible and relatively simple technique. In DPN, a material or 'ink' is coated onto an atomic force microscope (AFM) cantilever tip, generally by vapour-phase or solution-phase deposition. The ink is subsequently deposited from the AFM tip onto an appropriate substrate. Typically, there is a clear chemical or electrochemical driving force for transfer of the ink to the surface; for example, the chemisorption of alkanethiols onto a gold surface. The range of material systems to which DPN and related techniques have been applied has rapidly expanded since the first report of depositing thiols on gold surfaces,[2–4] to include patterning of proteins[5] and DNA[6] on gold surfaces, and metal salts,[7,8] metal oxides,[9] silazanes,[10,11] alkoxysilanes,[11,12] organic dyes,[13] dendrimers,[14] and polymers[15] on silicon oxide surfaces. Herein we describe a new functional ink based on trichlorosilane chemistry that is amenable to deposition by DPN onto silicon oxide. Additionally, we show this produces a versatile template that can direct subsequent deposition or growth of a variety of materials.

Lithography on insulating substrates at ever-shrinking scales is critical to the future development of electronic and sensor devices. DPN has been shown to provide a facile method for the serial patterning of silicon oxide surfaces. Ivanisevic and Mirkin[10] described the deposition of hexamethyldisilazane (HMDS) on Si and GaAs native oxide surfaces using DPN; however, HMDS is not amenable to further chemical functionalization after patterning. In order to pattern molecules on silicon oxide with DPN, Mirkin and co-workers have also created etch-resists based on self-assembled monolayers.[16,17] In this approach, a thin sacrificial layer of gold is deposited on a silicon oxide substrate, followed by patterning of a thiol on the gold by DPN. A final chemical etching step removes the unpatterned gold areas. More recent papers by Pena et al.[11] and Jung et al.[12] have explored the ability of DPN to write alkoxysilanes with functional end-groups that allow for further chemical modification. Pena et al. demonstrated the DPN of several trimethoxy and dimethoxy silanes with amine and mercaptan end-groups in registry with predefined photolithographically produced features. Similarly, Jung et al. deposited mercaptopropyltrimethoxysilane on glass via DPN and demonstrated further chemical modification of the mercaptan functionality with a biotin-labeled malemide.

In our studies, we have chosen 10-undecenyltrichlorosilane (UTCS) as the DPN 'ink' for several reasons. The choice of UTCS, or trichlorosilanes in general, allows the direct patterning of molecules on silicon oxide without the need for a solvent or elevated temperatures. Our approach results in the direct covalent attachment through only the headgroup of the silane, leaving the olefin-terminated tail (in the case of UTCS) available as a flexible starting point for further chemical modification. Possible modifications include the covalent or non-covalent growth of nanoparticles, conducting polymers, metal films, or biomolecules.

Although some authors have proposed that trichlorosilanes and alkoxysilanes would be unsuitable 'inks' for DPN[10] (due to possible decomposition or polymerization in the water meniscus that forms between the tip and surface), Pena et al.[11] and Jung et al.[12] have both found that deposition is possible in the case of alkoxysilanes. Given careful tip preparation, we have found that trichlorosilanes can also be written under appropriate conditions. Specifically, to achieve reproducible results, the silicon nitride AFM tips must be made hydrophobic prior to inking by first coating the tips with a silane layer. To remove any ambiguity as to the silane molecule deposited

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ADVANCED MATERIALS

from the AFM tip during writing, we pre-silylated the AFM tips with the *same* trichlorosilane molecule to be written. After pre-silylation, the tips were rinsed and stored in dichloromethane prior to use. To 'ink' the tips, they were removed from the dichloromethane, blown dry with nitrogen, dipped for 10 s in a solution of 10 mM UTCS in dichloromethane, and blown dry with difluoroethane.

The pre-silylated tips are very hydrophobic, which we believe suppresses the formation of a meniscus, allowing some compounds that are water sensitive to be deposited by DPN under atmospheric conditions with little decomposition or polymerization. This supposition is compatible with earlier observations[1,18–20] that AFM tips coated with hydrophobic molecules could suppress the formation of a meniscus, allowing for the imaging of partially formed water films on mica substrates. We note that hydrolysis or polymerization of some of the trichlorosilanes present on the tip is possible and even likely. However, the ability of trichlorosilanes to anchor through any (or all) of the three available chlorosilane bonds enables covalent bonding with the substrate even if some of the bonds are hydrolyzed or polymerized. We observed that tips coated with UTCS would write at a consistent rate for 2–3 h, and then deposition would abruptly stop, presumably because of polymerization and/or decomposition of the UTCS.

A topographic tapping-mode AFM image of UTCS deposited by DPN on a thermal silicon oxide surface is shown in Figure 1a, and a friction (LFM) image of a different pattern is shown in Figure 1b. The hydrophobic patterned area shows lower friction (darker) than the surrounding hydrophilic silicon oxide surface, as expected. Line widths of ~100 nm (Fig. 1a) are routinely attainable under the conditions we employed.

We find that UTCS can only be reproducibly deposited at relative humidities between ~30 % and 55 %. At lower relative humidities UTCS will not deposit, indicating that water plays an important role in this deposition. There is still an active discussion[19,21] as to the role of a water meniscus in the transport of hydrophobic 'inks'. Additionally, previous reports[22,23] suggest that production of a dense, well-ordered monolayer of octadecyltrichlorosilane (OTS) on SiO_x requires the use of extremely dry solvents, but also requires approximately one monolayer of water on the substrate. A more recent study[24] has shown that ultrasmooth monolayers of OTS can only be formed with very dry solvents, but the films take two days to grow. In contrast, in wet solvents, the OTS films grow much faster, but are rougher. Based on these studies, we expect the humidity to promote the reaction of the deposited chlorosilanes with the native oxide by maintaining monolayer water coverage on the substrate. However, at this time it is not clear to what extent the humidity promotes reaction relative to transport.

Our approach to forming chemical templates with UTCS is detailed in Figure 2. After patterning UTCS by DPN on an

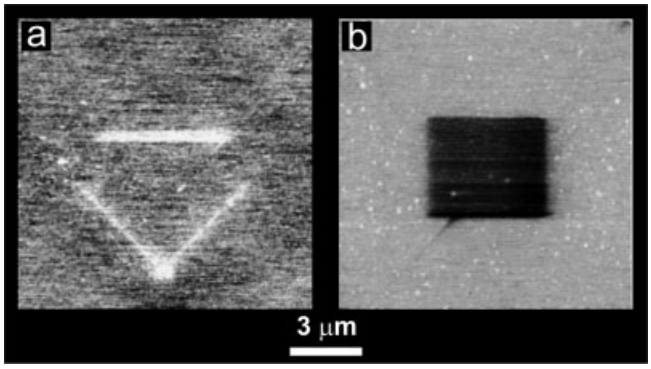

Figure 1. a) Tapping-mode AFM topographic image of UTCS patterned on silicon oxide. Apparent height of features is ~1 nm (root-mean-square roughness ~0.16 nm); b) LFM image of a UTCS patterned square, 5 μm × 5 μm, on silicon oxide.

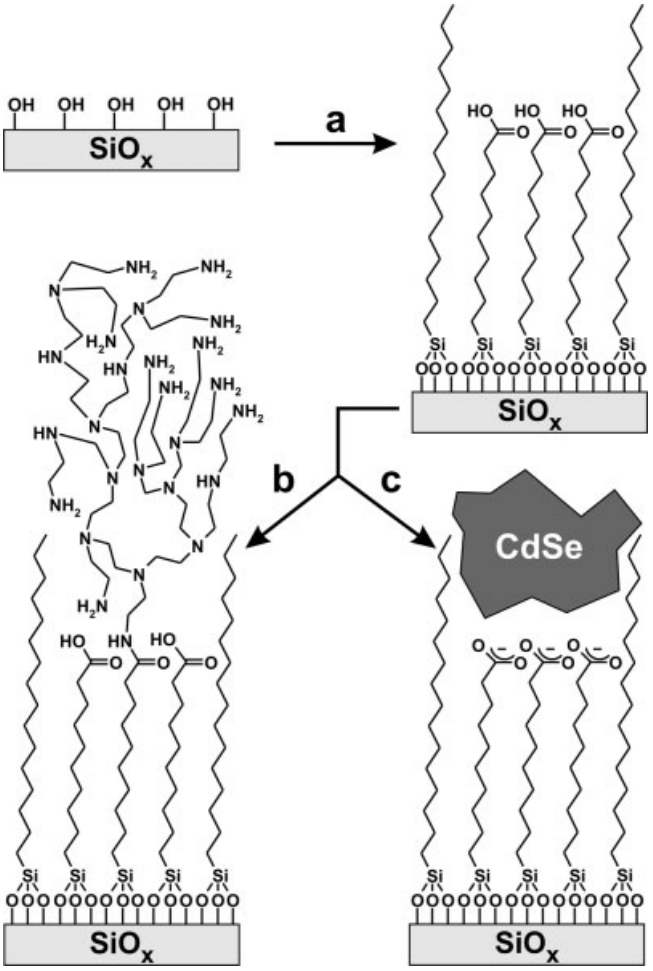

Figure 2. Idealized schematic diagram of procedures for preparation of flexible, reactive templates via DPN. a) Pattern fomation: i) deposition of 10-undecenyl trichlorosilane (UTCS) pattern via DPN, ii) back filling of unpatterned region with hexadecyl trichlorosilane, iii) oxidation of terminal olefin groups of 10-undecenyltrichlorosilane with $KMnO_4/KIO_3$ to form terminal carboxylic acid groups. b) Covalent attachement to patterned, oxidized template: i) activation of carboxylic acid groups with ethylchloroformate, ii) covalent coupling of PEI through reaction of primary amines with the activated carboxylic acid residing in the patterned area. c) Non-covalent growth through nucleation on patterned, oxidized template: i) deprotonation of carboxylic acid groups with dilute base, ii) electrostatic adsorption of Cd^{2+} ions onto patterned areas from solution, iii) reduction of adsorbed ions with H_2Se.

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ozone-cleaned, oxidized silicon substrate, the remaining unpatterned surface was passivated by immersion for 12 h in a 5 mM solution of hexadecyl trichlorosilane (HDTCS) in CH_2Cl_2. This procedure passivates the rest of the surface with a silane monolayer that resists non-specific adsorption and reaction during further chemical steps. After patterning and passivating, the terminal olefin groups of the UTCS layer can be oxidized in a buffered $KMnO_4/KIO_3$ solution to carboxylic acids, following the procedure of Wasserman et al.[25] As expected, the relative friction of the patterned area reverses due to the change in hydrophobicity after oxidation (not shown). Once the terminal olefins are oxidized, further chemical modification of the patterned area is possible through both covalent and non-covalent reactions.

To demonstrate the ability of the patterns to template materials through covalent modification, we have attached poly(ethylene imine) (PEI) to the patterned, oxidized area. To do so, we activate the carboxylic acid groups with ethyl chloroformate, and then couple PEI under basic conditions using the procedure of Wells and Crooks.[26] An example of such a covalent coupling is shown in Figure 3a.

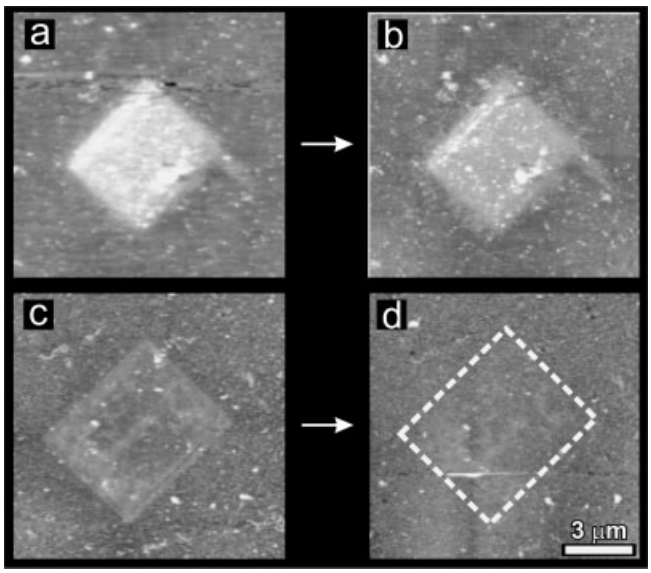

Figure 3. Tapping-mode AFM topographic images of covalent attachment of PEI to patterned, oxidized templates. a) After covalent attachment of PEI to the template through an ethyl chloroformate-mediated linkage. The apparent height of the pattern is 2 nm. b) Covalently attached PEI after attempts to remove it with solvents as described in the text. c) Electrostatically adsorbed PEI. d) Removal of electrostatically adsorbed PEI as described in the text (dashed box outlines underlying template).

The covalent attachment of PEI to the patterned silane area was confirmed by sonicating the sample in water, ethanol, THF, and dilute HCl, as shown by the results in Figure 3b. PEI that was covalently coupled to the silane surface in the patterned region was not removed during the consecutive sonication steps; however, the majority of the non-specifically adsorbed PEI in the unpatterned regions was removed with only an initial rinse in dilute HCl, as shown in Figure 3b. To further verify that this procedure results in covalent attachment of PEI, the patterned regions were exposed to PEI without the coupling agent (ethyl chloroformate). As shown in Figure 3c, the patterns lead to preferential deposition of PEI, presumably mediated by an electrostatic acid–base interaction between the acidic carboxylic acids in the pattern and the basic amines of PEI. PEI deposited without the coupling agent, however, was easily removed by a short sonication in dilute HCl (Fig. 3d), likely due to disruption of the acid–base interactions. Of the numerous solvents with which we attempted to remove the covalently attached PEI, only dilute base (KOH in water) was found to remove the patterned PEI. In this case, however, the deposited silane and potentially the topmost layers of the silicon oxide substrate itself are probably removed by basic hydrolysis.

Additional evidence of the covalent reaction of PEI with the underlying monolayer was obtained by repeating the same procedures used for covalent attachment to a patterned region on a silicon oxide attenuated total internal reflectance crystal (spectra not shown). We observed an increase and broadening of peaks in the hydrocarbon region of the infrared spectrum (ca. 2800–3000 cm^{-1}), attributable to the presence of PEI.[27] These additional features could not be removed with any of the procedures described above that were shown to remove adsorbed, unreacted PEI.

As indicated by the electrostatic attachment of PEI in the absence of coupling agent, the templates generated from the described trichlorosilane chemistries can also be used for non-covalent patterning. In a similar manner, we have grown semiconductor crystallites by deprotonating the carboxylic acid groups, electrostatically attaching metal ions (e.g., Pb^{2+} or Cd^{2+}), and reducing the adsorbed ions with H_2S or H_2Se (similar to procedures previously demonstrated for semiconductor nucleation on carboxylic acid terminated alkanethiols on gold[28]). Figure 4 displays the results of such an ion adsorp-

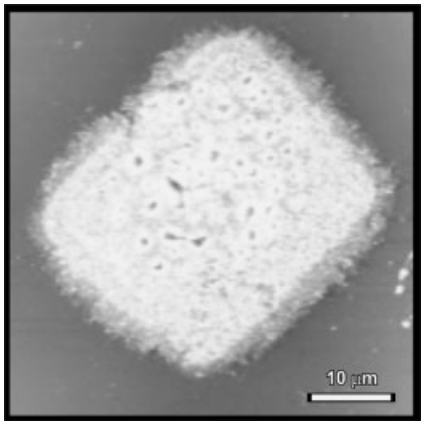

Figure 4. Tapping-mode AFM topographic image of non-covalent patterning of semiconductor films on patterned, oxidized templates. The bright feature in the image (apparent height ~22 nm) was produced by the adsorption of Cd^{2+} ions and subsequent reduction with H_2Se on a DPN patterned template.

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tion/reduction using Cd^{2+} as the metal ion and H_2Se as the reductant. Given the height of the structure, there is likely an excess of adsorbed Cd prior to reducing to CdSe. It is also possible that adventitious Cd adsorbs in the unpatterned areas and diffuses to the growing crystallite. Work is underway to understand the nucleation and growth of these structures.

In conclusion, we have shown that DPN can be used to directly pattern functional molecules on oxide substrates, and that the patterns produced can be used as versatile templates for the deposition or nucleation of additional materials. Further, we show that water-sensitive trichlorosilanes are amenable to patterning by DPN. We believe the patterned olefin/carboxylic acid groups could also be used to produce patterns of thiols,[29] silver films, other semiconductor nanoparticles, gold clusters, and organic multilayers, making this approach a flexible strategy for future applications of DPN.

Experimental

Materials: The following chemicals were used as received: polyethylenimine (M_w ca. 25 000, Aldrich), triethylamine (99.5 %, Aldrich), ethyl chloroformate (97 %, Aldrich), anhydrous dichloromethane (99.8 %, Aldrich), zinc selenide (99.9 %, Aldrich), hydrogen sulfide (99.5 %, Aldrich), potassium iodate (Mallinkrodt), cadmium chloride (79.8 %, Fischer), lead acetate (99 %, J.T. Baker), potassium permanganate (99+ %, Aldrich), hexadecyl trichlorosilane (Gelest) and 10-undecenyl trichlorosilane (Gelest). All solvents used were at least spectroscopic grade.

Preparation of Templates via DPN: The writing was performed in contact mode on a CP-Research atomic force microscope (AFM) (Veeco Instruments, Santa Barbara, CA) using silicon nitride microlevers (TM Microscopes, spring constant = 0.03 $N\,m^{-1}$) on thermal oxide silicon substrates. Typical writing speed was 0.2 $\mu M\,s^{-1}$ with a contact force of ~0.75 nN. Writing was typically performed under ambient laboratory conditions at ~23 °C and ~50 % relative humidity. Imaging was performed on the same instrument in either tapping/non-contact mode or in contact/lateral force microscopy mode, as noted. Contact/lateral force images were generally collected with the same UTCS-treated cantilevers used for deposition (with no apparent unintentional deposition occurring under typical imaging conditions).

Oxidation of Templates: After patterning, oxidation of 10-undecenyl trichlorosilane to the carboxylic acid was performed as described by Wasserman et al. [25]. Briefly, stock solutions of $KMnO_4$ (5 mM), KIO_4 (200 mM), and K_2CO_3 (20 mM) were prepared. Immediately prior to oxidation, a 1 mL aliquot of each stock solution was mixed with 7 mL of Millipore water. The patterned substrates were then immersed in this solution for 30–45 min and then removed and rinsed copiously with water and ethanol.

Covalent Attachment of Poly(ethylene imine) (PEI) to Patterned, Oxidized Templates: Patterned, oxidized templates were treated according to the procedure reported by Wells and Crooks [26] for covalently attaching amine terminated dendrimers to carboxylic acid terminated self-assembled monolayers. The patterned carboxylic acid surfaces were placed in 2 mL of dry dichloromethane with 4–5 drops of ethyl chloroformate and 2–3 drops of triethylamine for 2 h. The surface was then removed, rinsed with dichloromethane, and placed in a solution of 10 mM poly(ethylene imine) with 2–3 drops of triethylamine overnight. The substrates were then removed, rinsed, and sonicated in dichloromethane.

Non-Covalent Growth of Lead Sulfide and Cadmium Selenide Nanoparticles on Patterned, Oxidized Templates: Patterned, oxidized templates were dipped in a slightly basic ethanol solution to deprotonate the carboxylic acid groups, and subsequently placed in either a 5 mM lead acetate or 5 mM cadmium chloride solution for 15 min. Lead or cadmium ions electrostatically attach to the deprotonated carboxylic groups in the patterned areas as described by Jiang et al. [28]. Finally, after removing and rinsing the substrates with water and ethanol, the substrates were exposed to either a H_2S or H_2Se atmosphere (generated by adding water to ZnSe in the case of H_2Se or from a lecture bottle in the case of H_2S) for 10 min to complete the lead sulfide or cadmium selenide crystal/particle growth.

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[1] R. D. Piner, J. Zhu, F. Zu, S. Hong, C. A. Mirkin, *Science* **1999**, *283*, 661.
[2] X. Liu, L. Fu, S. Hong, V. P. Dravid, C. A. Mirkin, *Adv. Mater.* **2002**, *14*, 231.
[3] A. Ivanisevic, J.-H. Im, K.-B. Lee, S. J. Park, L. M. Demers, K. J. Watson, C. A. Mirkin, *J. Am. Chem. Soc.* **2001**, *123*, 12 424.
[4] L. M. Demers, C. A. Mirkin, *Angew. Chem. Int. Ed.* **2001**, *40*, 3069.
[5] D. L. Wilson, R. Martin, S. Hong, M. Cronin-Golomb, C. A. Mirkin, D. L. Kaplan, *Proc. Natl. Acad. Sci. USA* **2001**, *98*, 13 660.
[6] L. M. Demers, S. J. Park, T. A. Taton, A. Li, C. A. Mirkin, *Angew. Chem. Int. Ed.* **2001**, *40*, 3071.
[7] B. W. Maynor, Y. Li, J. Liu, *Langmuir* **2001**, *17*, 2575.
[8] Y. Li, B. W. Maynor, J. Liu, *J. Am. Chem. Soc.* **2001**, *123*, 2105.
[9] M. Su, X. Liu, S.-Y. Li, V. P. Dravid, C. A. Mirkin, *J. Am. Chem. Soc.* **2002**, *124*, 1560.
[10] A. Ivanisevic, C. A. Mirkin, *J. Am. Chem. Soc.* **2001**, *123*, 7887.
[11] D. J. Pena, M. P. Raphael, J. M. Byers, *Langmuir* **2003**, *19*, 9028.
[12] H. Jung, R. Kulkarni, C. P. Collier, *J. Am. Chem. Soc.* **2003**, *125*, 12 096.
[13] M. Su, V. P. Dravid, *Appl. Phys. Lett.* **2002**, *80*, 4434.
[14] R. McKendry, W. T. S. Huck, B. Weeks, M. Fiorini, C. Abell, T. Rayment, *Nano Lett.* **2002**, *2*, 713.
[15] A. Noy, A. E. Miller, J. E. Klare, B. L. Weeks, B. W. Woods, J. J. Deyoreo, *Nano Lett.* **2002**, *2*, 109.
[16] D. A. Weinberger, S. Hong, C. A. Mirkin, *Adv. Mater.* **2000**, *12*, 1600.
[17] H. Zhang, Z. Li, C. A. Mirkin, *Adv. Mater.* **2002**, *14*, 1472.
[18] Z. Q. Wei, C. Wang, C. L. Bai, *Surf. Sci.* **2000**, *467*, 185.
[19] J. Jang, G. C. Schatz, M. A. Ratner, *J. Chem. Phys.* **2002**, *116*, 3875.
[20] J. Schneider, W. Barger, G. U. Lee, *Langmuir* **2003**, *19*, 1899.
[21] P. E. Sheehan, L. J. Whitman, *Phys. Rev. Lett.* **2002**, *88*, 156 104.
[22] P. Silberzan, L. Leger, J. J. Benattar, *Langmuir* **1991**, *7*, 1647.
[23] D. L. Angst, G. W. Simmons, *Langmuir* **1991**, *7*, 2236.
[24] Y. Wang, M. Lieberman, *Langmuir* **2003**, *19*, 1159.
[25] S. R. Wasserman, Y.-T. Tao, G. M. Whitesides, *Langmuir* **1989**, *5*, 1074.
[26] M. Wells, R. M. Crooks, *J. Am. Chem. Soc.* **1996**, *118*, 3988.
[27] T. H. Ha, D. K. Kim, M. Choi, K. Kim, *J. Colloid Interface Sci.* **2000**, *226*, 98.
[28] P. Jiang, Z. Liu, S. Cai, *Langmuir* **2002**, *18*, 4495.
[29] S. Liu, R. Maoz, G. Schmid, J. Sagiv, *Nano Lett.* **2002**, *2*, 1055.

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