

# Dendrimer Monolayers as Negative and Positive Tone Resists for Scanning Probe Lithography

Marco Rolandi,<sup>†,§</sup> Itai Suez,<sup>†,§</sup> Hongjie Dai,<sup>\*,†</sup> and Jean M. J. Fréchet<sup>\*,†</sup>

*Department of Chemistry and Laboratory for Advanced Materials, Stanford University, Stanford, California 94305, Department of Chemistry, University of California, Berkeley, California 94720-1460 and Division of Material Sciences, Lawrence Berkeley National Laboratory, Berkeley, California 94720*

*Received February 24, 2004; Revised Manuscript Received March 29, 2004*

## ABSTRACT

A new scanning probe lithography scheme based on a self-assembled dendrimer monolayer on thin Ti films is presented. The method relies on the versatility of the functionalized dendrimer molecules to effectively function as etch resists by forming a densely packed self-assembled protective monolayer on a Ti film. Patterning of the Ti surface is accomplished using an AFM tip either as an ultra sharp scribe or as an electrical field point source to modify the monolayer. This, coupled to carefully selected etching conditions, allows the use of the dendrimer monolayers as both negative and positive tone resists. Facile formation of TiO<sub>2</sub> features ca. 25 nm wide and 12 nm tall on silicon oxide and ca. 50 nm wide gaps in a thin Ti film can easily be achieved. The dendrimer resist approach can be further developed in order to improve the minimum feature size to the single dendrimer molecule level.

Top down lithographic techniques for patterning and fabricating structures with resolutions in the range of a nanometer to tens of nanometers are indispensable to future device miniaturization. In addition to the classical Si/SiO<sub>2</sub> media used in microelectronic devices, high-resolution patterning of other substrates is also required for emerging applications in nanotechnology. Scanning probe lithography (SPL) is a promising approach for fabrication at the nanometer scale,<sup>1</sup> with high-resolution imaging capability that affords nanometer scale alignment accuracy for over layers. Extensive work has been carried out to explore the potential of nanolithographic writing using sharp probe tips with the atomic force microscope (AFM). The speed and throughput of AFM has been improved over the years with parallel operations of probe–tip arrays.<sup>2</sup> Impressive progress has been made in developing a wide variety of AFM nanolithography schemes, including field-enhanced oxidation,<sup>1–9</sup> organic polymer/dendrimer and self-assembled monolayer resist exposure,<sup>10–14</sup> mechanical plowing,<sup>15</sup> and dip-pen AFM lithography.<sup>16,17</sup> In particular, the speed and throughput of field-enhanced oxidation processes have been recently greatly improved by using a large three-dimensional conducting mask, either a DVD coated with metal or a TEM grid, that is directly in

contact with the surface instead of a single or array of cantilever probes.<sup>18,19</sup> This can effectively recreate the mask's pattern on the surface in a single simple exposure. Novel inorganic resist developments have also been recently made using thin molybdenum metal films as a sacrificial layer for SPL. The enhanced solubility of molybdenum oxide with respect to molybdenum in water has been exploited as a resist that can be fabricated via field-enhanced oxidation imaging.<sup>20</sup> A surprisingly underdeveloped area in SPL is the fabrication of nanostructures in thin titanium films. Titanium films patterned at the nanometer scale have several direct applications. Electrodes with nanometer gaps can be fabricated and used to measure single molecules or ultrashort channel nanotube FETs.<sup>21</sup> These devices can show effects such as Coulomb blockade and negative differential conductance, introducing them as good candidates for molecular electronics.<sup>22</sup> Moreover, posts of titanium oxide nanostructures developed with our negative tone approach can be used to create high surface area channels for organic semiconductor based solar cell devices.<sup>23</sup> While numerous attempts at field-enhanced oxidation of Ti films via SPL have been made,<sup>3,7,8,24</sup> nanolithography on Ti has proven to be a difficult task as the etch rates of both TiO<sub>2</sub> and Ti in a wet fluoride etchant (e.g., aqueous HF) are approximately the same. This hampers the capability of pattern transfer into underlying substrates and limits the utility of SPL based on Ti (or TiO<sub>2</sub>) resist. One solution is to protect the unpatterned Ti film by a self-

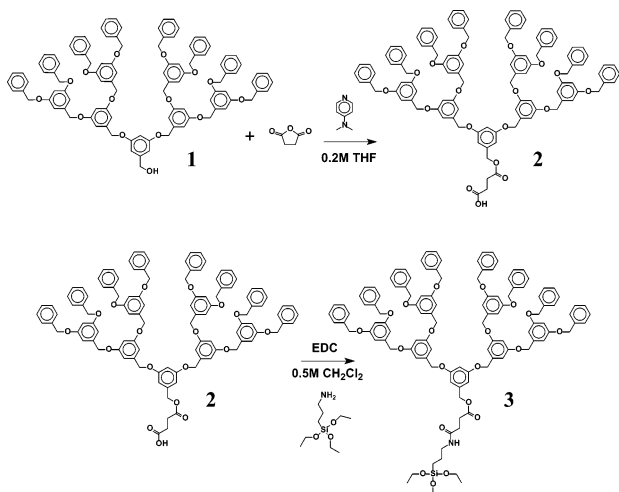
\* Corresponding authors. E-mail: frechet@cchem.berkeley.edu; hdai1@stanford.edu

<sup>†</sup> Stanford University.

<sup>‡</sup> University of California and LBNL.

<sup>§</sup> These authors contributed equally.

**Scheme 1.** Synthesis of Target Dendron (**3**), Attachment of the Triethoxysilane Functional Group to the Third Generation Poly(benzyl ether) Dendrimer



assembled monolayer (SAM) of organic molecules, such as octadecyltrichlorosilane (OTS) to enhance the resistance of Ti to a fluoride etch. However, the etch resistance imparted by commercially available organosilane SAMs is often insufficient for practical applications involving Ti/TiO<sub>2</sub> surfaces.<sup>24</sup>

Highly branched convergent dendrons<sup>25</sup> with appropriate end groups have shown high resistance to fluorine-based etchants for the patterning of Si,<sup>11,26</sup> their focal point can be modified with different functionalities to attach to the titanium surface. We have now designed a dendrimeric resist that may be deposited as a monolayer on the surface of a Ti film. Through both scribing and oxidation SPL techniques, we can produce both positive and negative tone pattern transfer into the underlying Ti film with sub-50 nm resolution. This is the first report of an SPL resist platform that can readily afford both positive and negative tone pattern transfer depending on the patterning technique employed. In addition, this is the first report of a self-assembled monolayer resist capable of obtaining sub-100 nm features in Ti films via SPL.

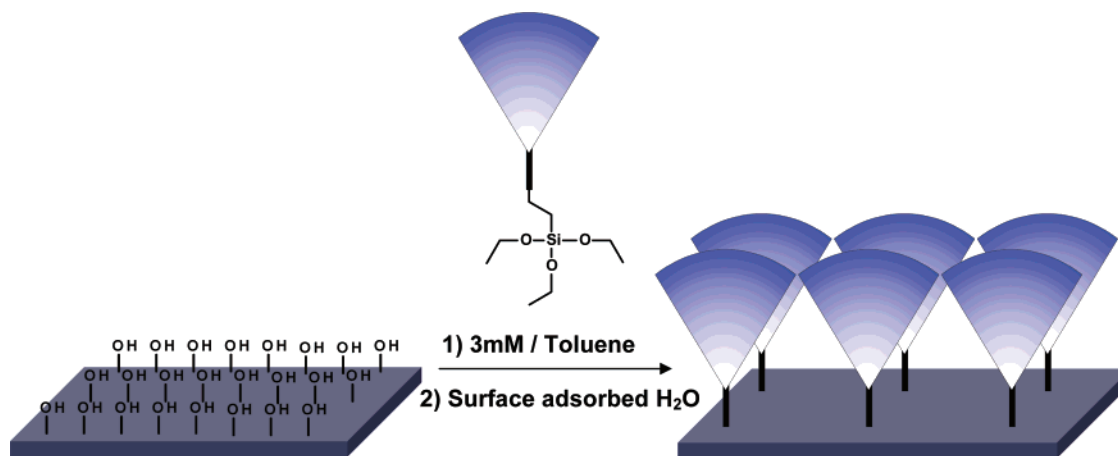
Convergent dendron (**3**) was used to form the highly stable self-assembled monolayer on the Ti surface. A triethoxysilane reactive group was chosen in this instance due to relative ease of monolayer self-assembly compared with more reactive silane functionalities such as chlorosilanes. Dendrimer (**3**) was synthesized as shown in Scheme 1 starting from the known third generation benzyl ether dendrimer (**1**).<sup>25</sup> Reaction of **1** with succinic anhydride using (dimethylamino)pyridine as the catalyst afforded intermediate **2**, which was coupled to (3-aminopropyl)triethoxysilane using 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) as the reagent to afford **3** as the main product. The dendrimer monolayer was then self-assembled on a thin film of Ti via covalent attachment between the triethoxysilane functional groups on the dendrimer and the surface hydroxyl groups on the native oxide of the Ti film (Figure 1). The formation of a single dendrimer monolayer on a thin Ti film was characterized by a liquid-phase quartz crystal microbalance (QCM) measurement. An average film thickness of 20 Å was evaluated by monitoring the change in mass per unit area

(from the raw QCM data) and dividing by the density of the material (Figure 2). Figure 2 shows the microbalance frequency stabilization for the first 25 min of analysis, at which time the dendrimer solution was injected into the crystal's environment and the mass change observed over the following 15 min could be correlated to surface coverage with a single monolayer.

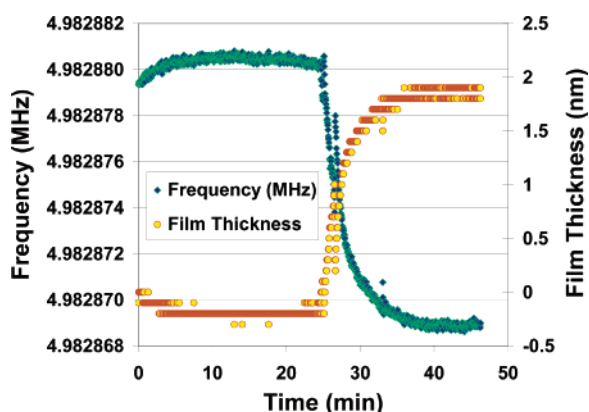
Our method of patterning is based on the surface modification of Ti thin films covered by the dendrimer monolayers using the sharp tips of an AFM. Figure 3 shows two different patterning schemes devised for dendrimer SAMs used as positive and negative tone resists, respectively. The samples were prepared by evaporating a 12 nm-thick Ti layer on top of a p-type Si(100) substrate with 500 nm thick thermally grown oxide. Lithographic field-enhanced oxidation, mechanical scribing of the surfaces, and imaging of the sample were all performed in the ambient (humidity 50–60%) with an AFM operating in the tapping mode. Heavily doped silicon cantilevers with integrated tips were used.

To image the Ti surface in the positive tone mode, a simple mechanical scribing process using the AFM tip to locally remove dendrimer molecules from the SAM was exploited, followed by a wet etching step to transfer the features into the underlying Ti film. For scribing, the vibration amplitude of the cantilever was reduced to 5% of the imaging value (~1 Å) while keeping the cantilever drive voltage constant. This affords soft contact between the AFM tip and the substrate, causing a slight bending of the cantilever and displacing the organic monolayer without damaging the Ti film or the tip. An AFM image of 35 nm wide lines scribed into the dendrimer monolayer at a scan rate of 4 μm/s is shown in Figure 4a. The depth of the lines, ca. 2 nm, is consistent with the thickness of the SAM as expected from the QCM measurements performed on the self-assembled dendrimer monolayer. The image was taken with the same tip used for scribing, showing minimum tip wear during the soft contact-mode mechanical scribing process.

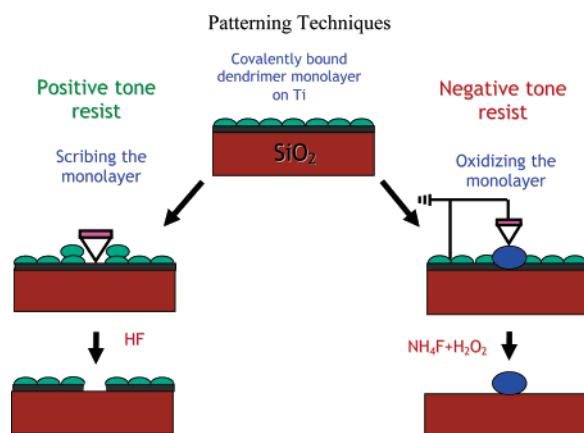
The patterned dendrimer SAMs on Ti were then etched using dilute aqueous HF as the etchant. Figure 4b shows an image of a sample after etching in a 0.1% HF solution for 51 s. The dendrimer monolayer resisted the HF etch, while the regions where the dendrimer molecules were mechanically removed by scribing showed deep depressions as a result of HF etching of the “deprotected” regions of the Ti film. Lines 50 nm wide etched to a depth of ca. 10 nm into the Ti film can be seen in Figure 4b. Such positive tone imaging with controlled etching was highly reproducible, indicating that the dendrimer SAM affords excellent etch resistance, effectively protecting the Ti surface it covers. In control experiments, bare Ti films without dendrimer SAM protection were completely etched away under the same HF etch treatment process. The quality of the Ti film remaining was determined by measuring the electrical properties of the dendrimer SAM protected Ti film before and after immersion in the HF solution. No change in electrical resistance was observed in this control experiment as a result of the etch resistance imparted by the dendrimer SAM. In contrast, bare Ti films without dendrimer SAM protection were completely removed under



**Figure 1.** Monolayer self-assembly of **3** on Ti substrate.



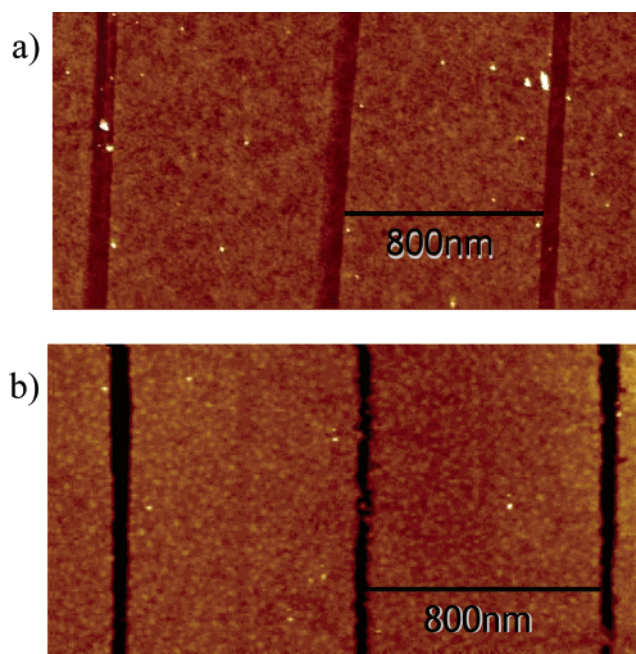
**Figure 2.** Monitoring the formation of a self-assembled monolayer of **3** on Ti substrate by quartz crystal microbalance (QCM).



**Figure 3.** Schematic representation of the dendrimer-coated Ti film with two alternative routes for imaging positive or negative tone patterns.

the same HF etching conditions, as confirmed by the observation of infinite electrical resistance due to the complete removal of the Ti film. Finally, contact angle measurements showed that after immersion in HF, the contact angle for SAM-covered Ti films decreased slightly from 80° to 70°, perhaps due to the presence of TiO<sub>2</sub> in the etched areas, but a value still higher than the contact angle of 62° measured for bare Ti.

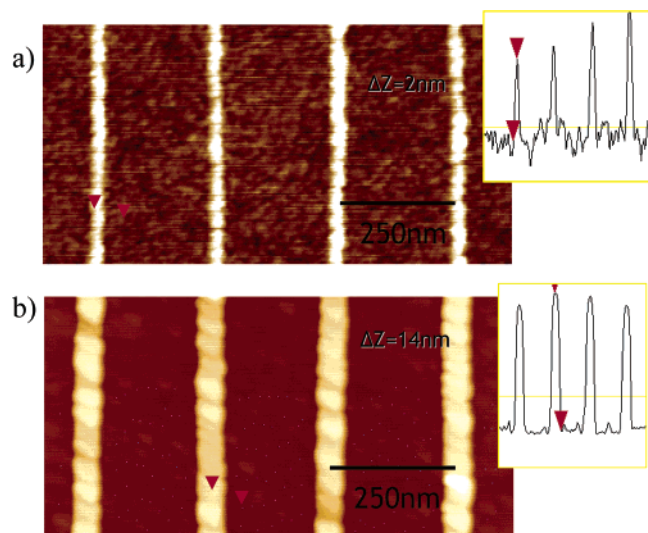
For patterning in the negative tone mode, the dendrimer SAMs were used in conjunction with a field-enhanced



**Figure 4.** AFM images of (a) 40 nm wide lines scribed into the dendrimer monolayer, (b) 50 nm wide trenches after etching the deprotected Ti in a 0.1%HF solution for 51 s.

oxidation approach. A positive bias was applied to the substrate while the negatively biased AFM tip traversed on the substrate along a designed path in a minimum 50% relative humidity environment. The vibration amplitude of the cantilever was set to at a constant 5–10 Å during writing to keep tip–sample proximity.<sup>1–3</sup> The scan rates and applied voltages varied, with best results for oxide formation being obtained at scan rates in the range of 0.4–1 μm/s and bias voltages between 10 and 12 V. Figure 5a shows a typical AFM image of the type of pattern obtained as a result of the local oxidation of the dendrimer–SAM covered Ti surface. The bright lines, presumably resulting from a field-enhanced oxidation of the Ti film, are 20 nm wide and 2 nm tall. The lines in the pattern were obtained with a scan rate of 1 μm/s with a bias voltage of 10 V using a 250 nm pitch. The patterned lines appear ~2 nm taller than the dendrimer monolayer background. Typically, the patterns become wider





**Figure 5.** AFM images of (a) 20 nm wide raised features produced via field-enhanced oxidation and (b) same lines after etching the film in 1 M  $\text{NH}_4\text{F}/\text{H}_2\text{O}_2$  solution for 12 min.

under higher bias voltages, lower scan speeds, or decreased tip–sample separation.

The patterned lines were found to resist etching in a 0.1 M  $\text{NH}_4\text{F}/\text{H}_2\text{O}_2$  solution for 12 min, while the rest of the Ti film blanketed by its dendrimer monolayer was completely etched by this treatment, as shown in Figure 5b. After completing the etching step, bright lines that were 40 nm wide and 14 nm tall were left on the substrate. The taller lines appear wider as a result of the tip convolution effect, calculated by assuming conical tip geometry with a 10 nm radius and a conical angle of  $20^\circ$ . The height difference of the lines before and after the etching step is consistent with essentially complete removal of the areas of the SAM/Ti film that had not been oxidized by the tip. The complete removal of dendrimer–SAM blanketed Ti by the 12 min etch in  $\text{NH}_4\text{F}/\text{H}_2\text{O}_2$  was also confirmed by comparing the electrical resistances of SAM/Ti samples before and after the 12 min etching step ( $\sim 400 \text{ } \Omega/\text{cm}$  and  $\gg 40 \text{ M}\Omega/\text{cm}$ , respectively).

For our dendrimer SAM coated Ti surfaces, we believe that the oxidation writing also converts the underlying Ti to  $\text{TiO}_2$ , as evidenced by the resulting taller features ( $\text{TiO}_2$ ) in areas affected by the tip. The fate of the dendrimer molecules on the Ti is less clear. It is possible that the strong electric field present between the tip and the substrate degrades the dendrimers and deposits a layer of amorphous carbon on the Ti film. This might create the hard mask we observed to be very resistant to the etching solution. Previously amorphous carbon deposition as a negative tone mask has been done using an electron beam from a scanning electron microscope.<sup>27</sup> It is possible that the electrons emitted from the AFM tip can produce a similar effect. The lines formed via field-enhanced oxidation on the dendrimer-coated Ti substrate are also insoluble in dilute HF. However, pattern transfer with dilute HF was not as sharp as that obtained with  $\text{NH}_4\text{F}/\text{H}_2\text{O}_2$ . Control experiments were performed using bare Ti films free of dendrimer coating. A slight etch selectivity in  $\text{NH}_4\text{F}/\text{H}_2\text{O}_2$  between oxidized Ti ( $\text{TiO}_2$ ) and the bare Ti film was found. However, the selectivity is quite

small and only allows for pattern transfer of 2 nm tall features (presumably  $\text{TiO}_2$ ). These results suggest that the material produced via oxidation of the dendrimer blanketed Ti film plays an essential role in imparting excellent etch resistance for negative tone pattern transfer.

In conclusion, we have devised new scanning probe lithography schemes based on a self-assembled dendrimer monolayer resist that enable the normally very difficult patterning of Ti surfaces. The excellent surface coverage afforded by the dendrimer resist is key to the imaging process. In future work we plan to explore the nature of the species that enable the formation of negative tone patterns. For positive tone imaging, better results might be obtained through the use of softer cantilevers and sharper tips. An even more exciting prospect derived from the use of dendrimer resists is the possibility that lithographic resolution may be improved to the level of single dendrimer molecules.

**Acknowledgment.** Financial support of this research by SRC-DARPA and by DOE-BES is acknowledged with thanks. The authors also thank Professor Calvin F. Quate (Stanford University) for many stimulating discussions.

**Supporting Information Available:** Experimental methods and analyses. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- Quate, C. F. *Surf. Sci.* **1997**, 386, 259.
- Minne, S.; Adams, J.; Yeralioglu, G.; Manalis, S.; Atalar, A.; Quate, C. *Appl. Phys. Lett.* **1998**, 73, 1742.
- Cooper, E. B.; Manalis, S. R.; Fang, H.; Dai, H.; Matsumoto, K.; Minne, S. C.; Hunt, T.; Quate, C. F. *Appl. Phys. Lett.* **1999**, 29, 3566.
- Dai, H.; Franklin, N.; Han, J. *Appl. Phys. Lett.* **1998**, 73, 1508.
- Dagata, J. A.; Schneir, J.; Harary, H. H.; Evans, C. J.; Postek, M. T.; Bennett, J. *Appl. Phys. Lett.* **1990**, 56, 2001.
- Snow, E.; Campbell, P. *Appl. Phys. Lett.* **1994**, 64, 1932.
- Matsumoto, K.; Ishii, M.; Segawa, K.; Oka, Y.; Vartanian, B. J.; Harris, J. S. *Appl. Phys. Lett.* **1996**, 68, 34.
- Dubois, E.; Bubenroff, J. L. *J. Appl. Phys.* **2000**, 87, 8148.
- Servat, J.; Gorostiza, P.; Sanz, F.; Perez-Murano, F.; Barniol, N.; Abadal, G.; Aymerich, X. *J. Vac. Sci. Technol. A* **1997**, 14(3), 1208.
- Wilder, K.; Quate, C. F.; Adderton, D.; Bernstein, R.; Elings, V. *Appl. Phys. Lett.* **1998**, 73, 2527.
- (a) Tully, D. C.; Wilder, K.; Fréchet, J. M.; Trimble, A.; Quate, C. F. *Adv. Mater.* **1999**, 11, 314. (b) Tully, D. C.; Fréchet, J. M. J. *Chem. Commun.* **2001**, 1229.
- Lercel, M.; Redinbo, G.; Craighead, H. G.; Sheen, C. W.; Allara, D. L. *Appl. Phys. Lett.* **1994**, 65, 974.
- Liu, G. Y.; Qian, Y. L. *Acc. Chem. Res.* **2000**, 33, 457.
- Sugimura, H.; Uchida, T.; Kitamura, N.; Masuhara, H. *J. Vac. Sci. Technol. B* **1994**, 12, 2884.
- Hu, S.; Hamidi, A.; Altmeyer, S.; Koster, T.; Spangenberg, B.; Kurz, H. *J. Vac. Sci. Technol. B* **1998**, 16, 2822.
- Piner, R.; Zhu, J.; Xu, F.; Hong, S.; Mirkin, C. A. *Science* **1999**, 283, 661.
- Li, Y.; Maynor, B.; Liu, J. *J. Am. Chem. Soc.* **2001**, 123, 2105.
- Hoeppener, S.; Maoz, R.; Sagiv, J. *Nano Lett.* **2003**, 3, 761.
- Cavallini, M.; Mei, P.; Biscarini, F. *Appl. Phys. Lett.* **2003**, 83, 5286.
- Rolandi, M.; Quate, C. F.; Dai, H. *Adv. Mater.* **2002**, 14, 191.
- Held, R.; Heinzel, T.; Studerus, P.; Ensslin, K.; Holland, M. *Appl. Phys. Lett.* **1997**, 71, 2689.
- Tour, J. M.; Reinerth, W. A.; Jones, L., II; Burgin, T. P.; Zhou, C.; Muller, C. J.; Deshpande, M. R.; Reed, M. A. *Ann. N.Y. Acad. Sci.* **1998**, 852, 197–204.
- O'Regan, B.; Grätzel, M. *Nature* **1991**, 353, 737–740.
- Sugimura, H.; Nakagiri, N. *J. Vac. Sci. Technol. A* **1996**, 14(3), 1223–1227.
- (a) Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1990**, 112, 7638. (b) Grayson, S. M.; Fréchet, J. M. J. *Chem. Rev.* **2001**, 101, 3819.

- (26) Tully, D. C.; Trimble, A. R.; Fréchet, J. M. J.; Wilder, K.; Quate, C. F. *Chem. Mater.* **1999**, *11*, 2892–2898.
- (27) Djenizian, T.; Santinacci, L.; Hildebrand, H.; Schmuki, P. *Surf. Sci.* **2003**, *524*, 40–48.
- (28) Neumann, A. W.; Good, R. J. *Surface and Colloid Science Vol. II: Experimental Methods*; Plenum Press: New York, 1979.

NL049700I