



Aliphatic dithiocarboxylic acids: New adsorbates for soft lithographic patterning

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^c d. y. l. d. n. p. g. l. f. v. n. i. d. r. n. F. t. r. n. F. t. r. n. 2. - . p.

ARTICLE INFO

Received 25 February 2008
Received in revised form 8 May 2008
Accepted 9 May 2008
Available online 15 May 2008

82.40.Np
82.45.Mp

Self-assembled monolayers
Dithiocarboxylic acids
Soft lithography

ABSTRACT

This paper describes an initial evaluation of the use of aliphatic dithiocarboxylic acids (ADTCAs) as transient protecting agents in soft lithographic patterning, also known as microcontact printing (μ CP). Surfaces micropatterned using ADTCA-based inks (**C10–C16**) were compared to that patterned using a standard hexadecanethiol ink. The patterns were characterized by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Etch-removal studies of SAM-coated gold substrates found that the longer chain-length ADTCAs (**C13–C16**) provide better protection against etching than the shorter chain-length ADTCAs (**C10–C12**). These studies demonstrate that ADTCA-derived SAMs can be used as effective resists for soft lithographic applications.

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1. Introduction

Self-assembled monolayers (SAMs) prepared from the adsorption of organic molecules onto metal surfaces have been extensively studied over the past two decades [1,2]. These organic thin films have potential applications in many areas, such as biomaterials fabrication [3], surface-patterning [4], and thin-film lubrication [5]. The most widely studied and easily prepared SAMs are those derived from the adsorption of normal alkanethiols on gold [1,2,6]. Researchers have shown that by using micro-contact printing (μ CP), patterned SAMs can be used to create detailed features on the surface of gold [7–10]. In fact, Lucent Technologies has reported the fabrication of microscopical devices with sub-micron features using this technique [11].

In μ CP, an elastomeric poly(dimethylsiloxane) (PDMS) stamp with a patterned relief structure on its surface is “inked” with an organic solution, which typically consists of a normal alkanethiol dissolved in ethanol. Bringing the inked stamp into contact with a

metal-coated substrate transfers the relief pattern to the substrate. The resultant SAM patterns are sufficiently stable to serve as resists (i.e., etch masks) for wet chemical etching of the metal surface. When a SAM-patterned metal-coated substrate is dipped into an aqueous solution of a chemical etchant (e.g., a mixture of potassium thiosulfate $K_2S_2O_3$ and potassium ferricyanide $K_4Fe(CN)_6$, the metal atoms that are not “protected” by the overlying alkanethiol adsorbate undergo rapid oxidation and dissolution [9]. Subsequent treatment with ultraviolet (UV) radiation can be used to remove the remaining SAM coating, exposing a metal pattern on the substrate surface. This metal pattern can serve as a microscopic circuit or can be coated with a semiconductor material to construct a miniature transistor.

There are additional patterning approaches that involve the use of SAMs for nanofabrication [4,12]. One of them is to oxidize normal alkanethiols on the surface of gold, activated by exposure to UV radiation through an overlying mask [4]. In this approach, the UV radiation initiates the conversion of the alkanethiolate headgroups into corresponding sulfonate groups. It is believed that photooxidation of the alkanethiolates proceeds via a two-stage mechanism involving cleavage of the C–S bond followed by oxidation of the sulfur headgroup [13]. However, the energy required for the bond breaking is high, and short-wavelength UV radiation is needed. It has been reported that 254 nm UV light [14] and 193 nm laser [4] can pattern normal alkanethiol SAMs on a

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gold surface. However, lengthy exposures are often required in these procedures.

In most cases, SAMs derived from the adsorption of n -alkanethiols ($\text{CH}_3(\text{CH}_2)_n\text{SH}$) on gold are stable under ambient laboratory conditions for weeks and can be difficult to remove for further processing. In contrast, we have found that SAMs derived from the adsorption of aliphatic dithiocarboxylic acid (ADTCA: $\text{CH}_3(\text{CH}_2)_{n-1}\text{CS}_2\text{H}$) on gold provide initially robust films that degrade rapidly under mild conditions [15,16]. Our previous studies evaluated the stability of ADTCA-based SAMs as a function of chain length under various external stimuli [16]. These studies found that the desorption of the ADTCA SAMs is chain-length dependent, and the presence of oxygen enhances the rate of desorption. Importantly, SAMs derived from ADTCAs can be more easily removed from the surface of gold than can SAMs derived from n -alkanethiols [16]. Given these encouraging findings, we chose to further explore the use of ADTCA-based SAMs in surface-patterning technologies [17].

To this end, we examine here the etch resistance of ADTCA SAMs on plasma-cleaned gold substrates by comparing patterned SAMs derived from ADTCAs having the formula $\text{CH}_3(\text{CH}_2)_{n-1}\text{CS}_2\text{H}$, where $n = 9-15$, to those derived from the longest corresponding n -alkanethiol, hexadecanethiol (**HDT**), $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$. The quality of the initial SAMs was evaluated using static contact angle measurements. Additional studies employed scanning electron microscopy (SEM) and atomic force microscopy (AFM) to evaluate the etch resistance of the SAMs in a ferri/ferrocyanide etching solution. Taken together, our studies find that the use of ADTCAs as organic inks offers alternative strategies and potential improvements in μCP -based applications.

2. Experimental procedures

A description of many of the materials and procedures presented in this study can be found in previous reports

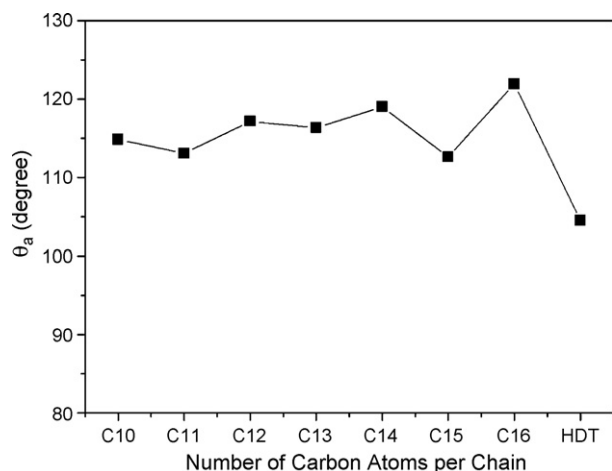


Fig. 1. Static contact angles of water on SAMs derived from **C10–C16** ADTCAs and **HDT**.

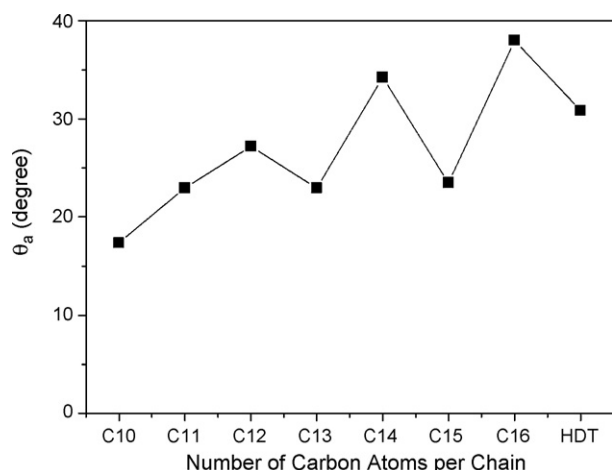


Fig. 2. Static contact angles of hexadecane on SAMs derived from **C10–C16** ADTCAs and **HDT**.

which were substantially thinner than those employed in the previous studies. Furthermore, the gold substrates utilized here were stored and aged for approximately 6 months before use. We note also that Tsai and Lin [19], and Rubinstein et al. [21,22] reported that the preconditioning of gold substrates affects the organization of SAMs. Although pretreatment with oxygen plasma followed by rinsing in absolute ethanol is typically a reliable process for the preparation of reliable gold surfaces, alkanethiol

Table 1

Time required for complete removal of uncoated and SAM-coated gold

Substrates	Time for Au removal (min)
Bare gold (150 nm Au + 30 nm Cr)	40
C10 on Au	98
C11 on Au	115
C12 on Au	105
C13–C16 on Au	>180
HDT on Au	140

monolayers absorbed on gold surfaces are sensitive to various treatment parameters [22], which can lead to diminished contact angle values. In this report, we made no effort to optimize the oxygen plasma treatment of the gold surface.

. . . P γ d d , p t γ r d d d r r r n r n s f y i s n γ d n n f

After stamping the gold slides with a micropatterned and “inked” PDMS stamp, the slides were immersed in the etching solution for 40 min to remove gold from the unprotected areas. Analysis by SEM revealed that both **HDT** and the **C16** ADTCA serve as efficient etch resists under the selected conditions (see Fig. 3). The images in Fig. 3, however, lack sufficient resolution to allow us to conclusively identify which type of adsorbate (ADTCA vs. *n*-alkanethiol) offers better edge resolution in μ CP. Consequently, we undertook additional experiments in an effort to distinguish their general micropatterning effectiveness.

In separate experiments, we compared the etch resistance of various SAM-coated slides by immersing the samples in etching solutions until the gold layer was completely removed as judged by visual examination. The etching solutions were completely refreshed every 40 min to maintain their activity. The results are listed in Table 1. Without any SAM protection, the gold substrates were completely removed by the ferri/ferrocyanide etching solution in 40 min. For ADTCAs having longer chain lengths (**C13–C17**), the time required for etching the gold layer was longer than 180 min; in contrast, that required for ADTCAs having shorter chain lengths (**C10–C12**) varied from 98 min to 115 min. For comparison, **HDT** can protect the gold layer against the etching solution for 140 min. These results are consistent with the general trend observed for *n*-alkanethiols on gold [20,23]; namely, that SAMs with longer chain lengths provide enhanced etch resistance compared to SAMs with shorter chain lengths.

We further evaluated the etch resistance and edge resolution of μ CP ADTCA patterns on gold using AFM. These experiments utilized 10 mM ethanolic solutions of the ADTCAs as inks. The PDMS stamp was immersed in the ink for 30 s, blown dry with a

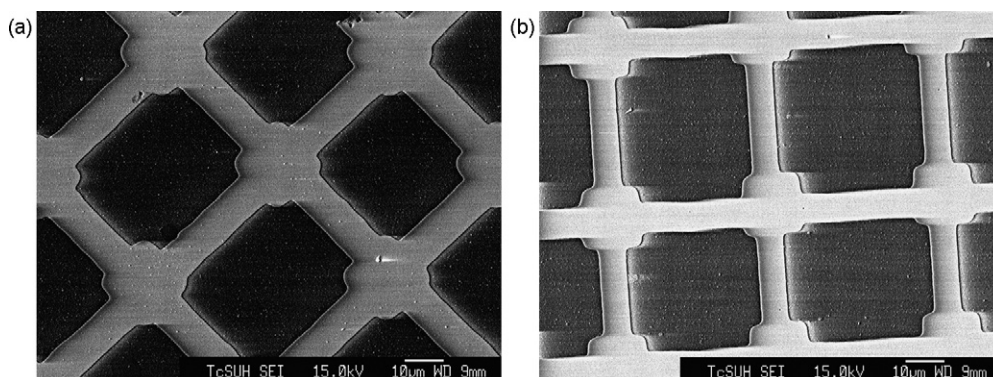


Fig. 3. SEM images of etched gold surface patterned using (a) hexadecanethiol and (b) dithiohexadecanoic acid.

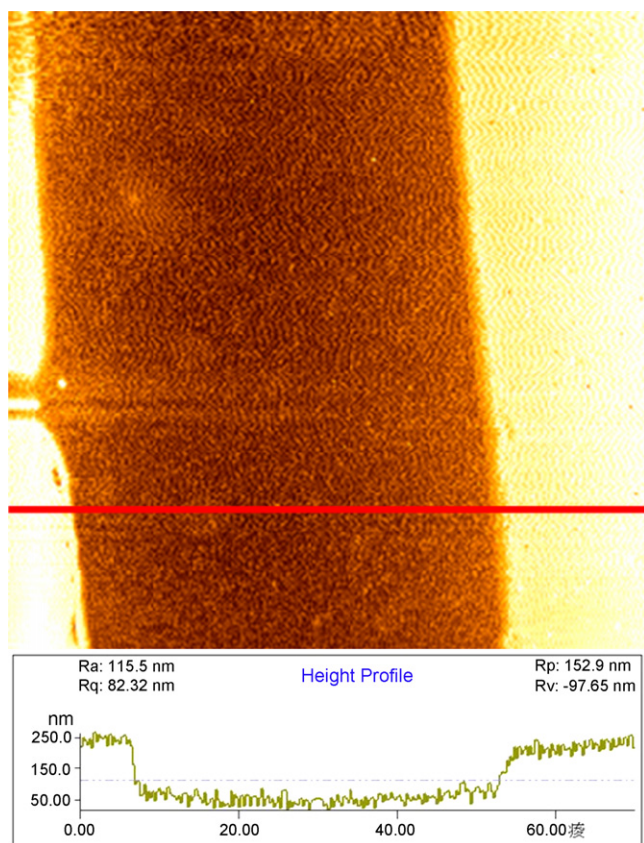


Fig. 4. AFM image of μ CP gold patterns protected by **C16** ADTCA SAMs. The height profile of the corresponding line scan (red line) is shown below. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

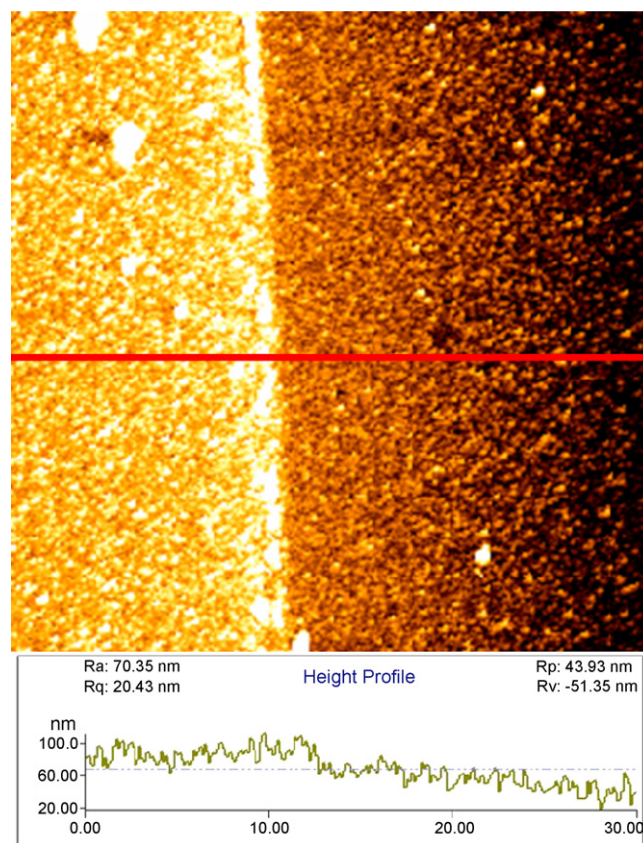


Fig. 5. AFM image of μ CP gold patterns protected by **C13** ADTCA SAMs. The height profile of the corresponding line scan (red line) is shown below. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

stream of nitrogen, and then contacted with the plasma-cleaned gold surface for 15 s. The patterned gold substrates were subsequently soaked in etching solution for 40 min. The edges of protected and unprotected gold were then examined using AFM. Figs. 4 and 5 illustrate the top view of the gold patterns protected by **C16** and **C13** ADTCA SAMs, respectively. The corresponding height profiles generated from line scans (marked red on the figures) of the AFM images are also shown. From the line scans, the height differences of the gold patterns covered by the **C16** and **C13** ADTCA SAMs are 165 nm and 32 nm, respectively, corresponding to the remaining gold thicknesses after wet chemical etching. Given that the gold substrates consisted of 150 nm of gold deposited on 30 nm of chromium deposited on a silicon wafer, the **C16** ADTCA SAM appears to offer better protection against the etchant than does the **C13** ADTCA SAM, which is consistent with the time-dependent etch-removal trends described above and the etching vs. chain-length trends observed for ω -alkanethiols on gold [20,23].

Importantly, the edges of the gold patterns are sharper for the **C16**-derived samples than are those for the **C13**-derived samples. For μ CP with ω -alkanethiols, the mobility of the thiol molecules plays an important role in determining the edge sharpness of the surface patterns, where the shorter molecules diffuse laterally more readily, leading to poorly defined edges [24]. This hypothesis appears also to be true for gold surfaces micropatterned with ADTCA adsorbates. The good etch resistance of the **C16** ADTCA, coupled with its facile removal under ambient laboratory conditions [16], offers new strategies for generating multicomponent patterned interfaces. Additional investigations are currently being pursued.

4. Conclusions

Etch-removal studies of SAM-coated gold substrates showed that the longer chain-length ADTCA SAMs (**C13**–**C16**) offer better protection against etching than the shorter chain-length analogs (**C10**–**C12**). Given the information from the contact angle studies indicating that the tailgroups of the SAMs generated from the shorter ADTCAs are more disordered than are those generated from longer ADTCAs, it is plausible that the shorter ADTCAs undergo relatively rapid breakdown via facile diffusion of the etchant through the disordered films, and thus the etch-removal of gold is accelerated relative to that observed for the better-ordered long-chain analogs. Independent measurements by AFM of feature sharpness on micropatterned gold substrates suggested that the **C13** ADTCA diffuses laterally during the μ CP process, leading to poorly resolved edge features compared to those obtained using the longer **C16** ADTCA. As a whole, this study demonstrates that ADTCs can serve as useful inks in soft lithographic patterning.

Acknowledgments

This research was supported by the National Science Council of Taiwan under contract numbers NSC 92-2218-E-194-012 and NSC 94-2214-E-194-010. The work at the University of Houston was supported by the Robert A. Welch Foundation (Grant E-1320).

References

- [1] A. Ulman, Chem. Rev. 96 (1996) 1533–1554.

- [2] J.C. Love, L.A. Estroff, J.K. Kriebel, R.G. Nuzzo, G.M. Whitesides, *Chem. Rev.* 105 (2005) 1103–1169.
- [3] M. Mrksich, G.M. Whitesides, *Annu. Rev. Biophys. Biomol. Struct.* 25 (1996) 55–78.
- [4] S. Friebe, J. Aizenberg, S. Abad, P. Wiltzius, *Appl. Phys. Lett.* 77 (2000) 2406–2408.
- [5] J.-B.D. Green, M.T. McDermott, M.D. Porter, L.M. Siperko, *J. Phys. Chem.* 99 (1995) 10960–10965.