

Templated Electrochemical Deposition of Zirconia Thin Films on “Recordable CDs”

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In this paper, we describe a practical method of using gold films constructed from recordable compact disks (CD-Rs) as simple, inexpensive, and micropatterned conductive substrates for the fabrication of inorganic material microstructures. Extending from their application for the fabrication of self-assembled monolayers (SAMs) reported recently, bare and SAM-modified CD-R gold substrates have been used for template-directed electrodeposition of zirconia (ZrO₂) thin films (i.e., the controlled formation of zirconia thin films on the different areas of the prefabricated, micrometer mountain–valley CD-R gold substrate surfaces). The present results demonstrate that the variation of the functional groups of the selected SAMs combined with electrodynamic control can be very successful to “customize” the formation and microstructure of functional inorganic thin films, which hold promise for modern technological applications.

Recently, we have established an easy, inexpensive, and reproducible method to prepare self-assembled monolayers (SAMs) of long-chain alkanethiols on gold substrates prepared from recordable compact disks (CD-Rs) after removing the protective polymer films with concentrated nitric acid.¹ Wetting measurements, electrochemistry, infrared spectroscopy, and scanning tunneling microscopy show no distinct differences between these organic monolayers and the SAMs formed by traditional methods.^{2–4} This approach also avoids the use of a dangerous bath of H₂SO₄ and H₂O₂ (so-called “piranha solution”) that is required for cleaning substrates prepared by vacuum deposition or sputtering.¹ Meanwhile, Angnes and co-workers have pioneered the use of gold electrodes from CD-Rs in their studies of electroanalytical chemistry.^{5–8} Daniel et al. have fabricated thin-layer spectroelectrochemical cells using a similar type of gold electrodes from CD-

Rs.⁹ Independently, Westbroek et al. have constructed flow-through cells using CDrodes for on-line amperometric determination of Ce(IV) during polymerization reactions.¹⁰ In this report, we demonstrate the application of these unique gold substrates to pattern metal oxide thin films, aiming at the development of knowledge regarding the fabrication of functional inorganic thin films ranging from micro- to nanostructures. In particular, we describe the controlled electrodeposition of zirconia thin films on the different areas of the prefabricated, micrometer mountain–valley CD-R gold substrate surfaces.

The fabrication of material micro- to nanostructures is important primarily because of the potential applications in modern technologies, such as microelectromechanical, microelectronic, and other miniature devices.^{11–13} Particularly, the ability to pattern functional inorganic thin films into useful device architectures is key to applications in the area of electrochromics and photocatalysis as well as batteries and fuel cells.¹⁴ By taking advantage of both lithography techniques (to prepare the surface patterns)^{15–19} and organic modification (to functionalize solid substrate surfaces with SAMs for biomimetic processing),^{20,21} patterning inorganic materials into desired micro- to nanostructures has been very successful. In addition to the photolithography technique,^{15–17} microcontact printing (μ -CP) is another convenient method that uses a patterned elastomer (usually polydimethylsiloxane, PDMS) as the mold, stamp, or mask to generate or transfer chemical patterns.^{22–27} Its enormous capabilities have been demonstrated,

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- (1) Yu, H. Z. *Anal. Chem.* **2001**, *73*, 4743.
 - (2) Badia, A.; Lennox, R. B.; Reven, L. *Acc. Chem. Res.* **2000**, *33*, 475.
 - (3) Chechik, V.; Crooks, R. M.; Stirling, C. M. *J. Adv. Mater.* **2000**, *12*, 1161.
 - (4) Ulman, A. *Chem. Rev.* **1996**, *96*, 1533.
 - (5) Angnes, L.; Richter, E. M.; Augelli, M. A.; Kume, G. H. *Anal. Chem.* **2000**, *72*, 5503.
 - (6) Richter, E. M.; Kume, G. H.; Mioshi, R. N.; Angnes, L.; Augelli, M. A. *Fresenius' J. Anal. Chem.* **2000**, *366*, 444.
 - (7) Muñoz, R. A. A.; Matos, R. C.; Angnes, L. *Talanta* **2001**, *55*, 855.
 - (8) Richter, E. M.; Augelli, M. A.; Magarotto, S.; Angnes, L. *Electroanalysis* **2001**, *13*, 760.

- (9) Daniel, D.; Gutz, I. G. R. *Electroanalysis* **2001**, *13*, 681.
- (10) Westbroek, P.; De Strycker, J.; Dubruel, P.; Temmerman, E.; Schacht, E. H. *Anal. Chem.* **2002**, *74*, 915.
- (11) Jackman, R. J.; Brittain, S. T.; Adams, A.; Prentiss, M. G.; Whitesides, G. M. *Science* **1998**, *280*, 2089.
- (12) Payne, D. A.; Clem, P. G. *J. Electroceram.* **1999**, *3*, 163.
- (13) Jacobs, H. O.; Whitesides, G. M. *Science* **2001**, *291*, 1763.
- (14) Granqvist, C. G. *Handbook of Inorganic Electrochromic Materials*, 1st ed.; Elsevier: Amsterdam, 1995.
- (15) Koumoto, K.; Seo, S.; Sugiyama, T.; Seo, W. S.; Dressick, W. J. *Chem. Mater.* **1999**, *11*, 2305.
- (16) Masuda, Y.; Jinbo, Y.; Yonezawa, T.; Koumoto, K. *Chem. Mater.* **2002**, *14*, 1236.
- (17) Saito, N.; Haneda, H.; Sekiguchi, T.; Ohashi, N.; Sakaguchi, I.; Koumoto, K. *Adv. Mater.* **2002**, *14*, 418.
- (18) Jeon, N. J.; Clem, P. G.; Nuzzo, R. G.; Payne, D. A. *J. Mater. Res.* **1996**, *10*, 2996.
- (19) Clem, P. G.; Jeon, N. L.; Nuzzo, R. G.; Payne, D. A. *J. Am. Ceram. Soc.* **1997**, *80*, 2821.
- (20) Bunker, B. C.; Rieke, P. C.; Tarasevich, B. J.; Campbell, A. A.; Fryxell, G. E.; Graff, G. L.; Song, L.; Liu, J.; Virden, J. W.; McVay, G. L. *Science* **1994**, *264*, 48.
- (21) Niesen, T. P.; Bill, J.; Aldinger, F. *Chem. Mater.* **2001**, *13*, 1552.
- (22) Xia, Y.; Rogers, J. A.; Paul, K. E.; Whitesides, G. M.; *Chem. Rev.* **1999**, *99*, 1823, and references therein.

particularly in creating chemical templates for inorganic material microfabrication.^{22–27} Recently, an alternative fabrication procedure for preparing material microstructures has been developed in which prefabricated substrates were used for selective growth of nanotubes or colloidal crystal,^{28–30} and electrodeposition of metal oxide thin films and noble metals.^{31–33} The selection and preparation of micropatterned substrates and the fine control of the reaction condition are critical issues for consideration.

As shown in Figure 1a, gold substrates prepared from CD-Rs show a unique pregrooved feature that consists of uniform mountain–valley strips at the micrometer level. This offers a micropatterned conductive substrate that is simple, inexpensive, and convenient for the study of selective crystal growth or electrodeposition of metal oxide films. We chose zirconia thin films as the first system to study not only for the practical applications as solid-state electrolytes for fuel cells, oxygen sensors, and catalysts^{34–36} but also for the primary research that has been amended regarding the aqueous synthesis and electrodeposition of zirconia thin films at controlled conditions.^{37–40} Recently, SAMs on gold were explored to promote the electrochemical formation of microcrystalline zirconia.^{41,42} Organic monolayer modified silicon crystals were also used for aqueous deposition of ZrO_2 or Y_2O_3 -doped ZrO_2 thin films.^{43,44}

EXPERIMENTAL SECTION

11-Mercapto-1-undecanol (97%), 11-mercaptoundecanoic acid (95%), and 1-dodecanethiol (98%) were used as received from Aldrich (Milwaukee, WI). CD-Rs (Kodak CD-R Gold Ultima) were obtained locally. The water used was deionized with a Milli-Q purification system (Millipore Products, Bedford, MA). Other chemicals were of ACS reagent grade and were used without further purification.

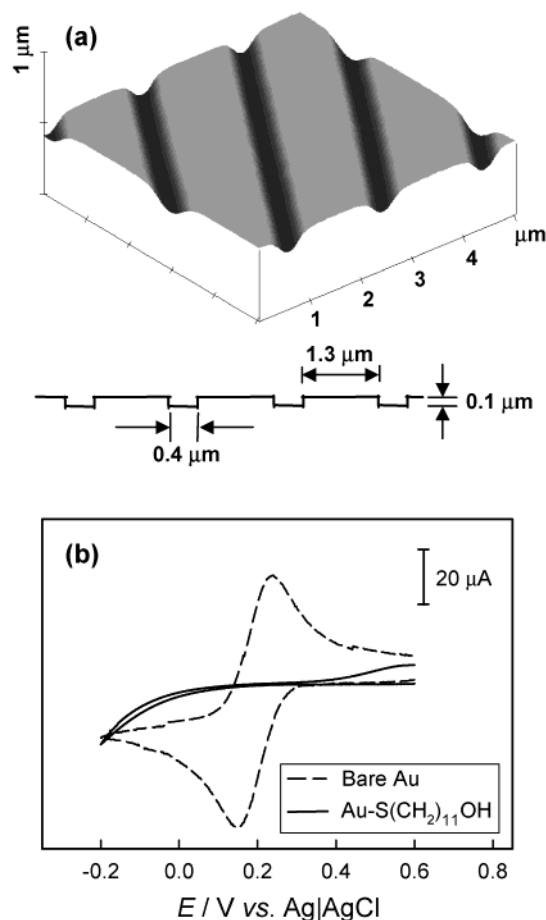


Figure 1. Microscopic morphology and electrochemical response of gold substrates prepared from CD-Rs. (a) AFM image of the pregrooved features of CD-R gold substrates and the schematic cross-sectional profile. (b) Cyclic voltammograms for bare gold from CD-Rs (---) and $\text{Au-S(CH}_2\text{)}_{11}\text{OH}$ (—) in 1.0 mM $\text{K}_3\text{Fe(CN)}_6$ and 0.1 M KCl. A scan rate of 50 mV/s was employed.

Before use in experiments, the CD-Rs were cut into conveniently sized slides with a pair of scissors. These pieces were then immersed in concentrated HNO_3 for 3–5 min to remove the protective polymer film, and then rinsed with copious amounts of water. The SAMs were prepared by immersing the fresh gold substrates into dilute thiol solutions (~ 1.0 mM) in ethanol for 18–24 h.¹ The gold substrates modified with SAMs were rinsed sequentially with 95% ethanol and water, then dried under N_2 prior to further derivatization or characterization.

Cyclic voltammetry was performed using an EG&G model 263 potentiostat/galvanostat that was interfaced to a computer with an IEEE 488 board. Bare or modified CD-R gold substrates were used as working electrodes (0.69 cm^2). Typically, zirconia thin films were formed by cycling at a scan rate of 20 mV/s for 10 cycles from -1.1 V to $+0.7$ V in an aqueous solution of 5.0 mM $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and 0.1 M KCl. The prepared samples were rinsed gently with water and dried with N_2 prior to the microscopic imaging. All electrode potentials were reported with respect to an Ag|AgCl|3 M NaCl reference electrode. A Pt wire was used as the counter electrode.

Scanning electron microscopy (SEM) was carried out using a JEOL JSM-5900 LV machine. All samples were imaged under vacuum conditions using secondary electron imaging (SEI). The

- (23) Finnie, K. R.; Haasch, R.; Nuzzo, R. G. *Langmuir* **2000**, *16*, 6968.
- (24) Jeon, N. L.; Nuzzo, R. G.; Xia, Y.; Mrksich, M.; Whitesides, G. M. *Langmuir* **1995**, *11*, 3024.
- (25) Azzaroni, O.; Schilardi, P. L.; Salvarezza, R. C. *Nano Lett.* **2001**, *1*, 291.
- (26) Qin, D.; Xia, Y.; Xu, B.; Yang, H.; Zhu, C.; Whitesides, G. W. *Adv. Mater.* **1999**, *11*, 1433.
- (27) Ji, J. M.; Li, X.; Canham, L. T.; Coffey, J. L. *Adv. Mater.* **2002**, *14*, 41.
- (28) Kumacheva, E.; Golding, R. K.; Allard, M.; Sargent, E. H. *Adv. Mater.* **2002**, *14*, 221.
- (29) Bae, E. J.; Choi, W. B.; Jeong, K. S.; Chu, J. U.; Park, G. S.; Song, S.; Yoo, I. K. *Adv. Mater.* **2002**, *14*, 277.
- (30) Bao, J. C.; Tie, C. Y.; Xu, Z.; Zhou, Q. F.; Shen, D.; Ma, Q. *Adv. Mater.* **2001**, *13*, 1631.
- (31) Stevenson, K. J.; Hurrst, G. J.; Hupp, J. T. *Electrochem. Solid State Lett.* **1999**, *2*, 175.
- (32) Djenizian, T.; Santinacci, L.; Schmuki, P. *App. Phys. Lett.* **2001**, *78*, 2940.
- (33) Djenizian, T.; Santinacci, L.; Schmuki, P. *J. Electrochem. Soc.* **2001**, *148*, C197.
- (34) Mori, M.; Abe, T.; Itoh, H.; Yamamoto, O.; Takeda, Y.; Kawahara, T. *Solid State Ionics* **1994**, *74*, 157.
- (35) Can, Z. Y.; Narita, H.; Mizusaki, J.; Tagawa, H. *Solid State Ionics* **1995**, *79*, 344.
- (36) Miller, T. M.; Grassian, V. H. *J. Am. Chem. Soc.* **1995**, *117*, 10969.
- (37) Yao, T.; Inui, T.; Ariyoshi, A. *J. Am. Ceram. Soc.* **1996**, *79*, 3329.
- (38) Matsui, K.; Ohgai, M. *J. Am. Ceram. Soc.* **1997**, *80*, 1949.
- (39) Gal-Or, L.; Silberman, I.; Chaim, R. *J. Electrochem. Soc.* **1991**, *138*, 1939.
- (40) Chaim, R.; Silberman, I.; Gal-Or, L. *J. Electrochem. Soc.* **1991**, *138*, 1942.
- (41) Bandyopadhyay, K.; Vijayamohan, K. *Langmuir* **1998**, *14*, 6924.
- (42) Aslam, M.; Pethkar, S.; Bandyopadhyay, K.; Mulla, I. S.; Sainkar, S. R.; Mandale, A. B.; Vijayamohan, K. *J. Mater. Chem.* **2000**, *10*, 1737.
- (43) Agarwal, M.; De Guire, M. R.; Heuer, A. H. *J. Am. Ceram. Soc.* **1997**, *80*, 2967.
- (44) Polli, A. D.; Wagner, T.; Fischer, A.; Weinberg, G.; Jentoft, F. C.; Schlögl, R.; Rühle, M. *Thin Solid Films* **2000**, *379*, 122, and references therein.

typical accelerating voltage of the electron beam used was 10 kV, and the typical magnification setting was $\times 5000$. All samples were grounded with pieces of copper tape to curtail specimen charging.

Atomic force microscopy (AFM) was performed using a Digital Instruments Multimode Nanoscope III. The images were acquired at 1 Hz in contact mode using Si_3N_4 -sharpened tips (Digital Instruments, $0.12 \text{ N}\cdot\text{m}^{-1}$) at a constant force of $1\sim 2 \text{ nN}$, and were leveled but unfiltered.

RESULTS AND DISCUSSIONS

Before the electrochemical deposition of zirconia thin films, freshly prepared CD-R gold substrates and those modified with 11-mercaptoundecanol SAMs ($\text{Au-S(CH}_2\text{)}_{11}\text{OH}$) were examined using cyclic voltammetry. In Figure 1b, the dashed and solid lines show the current–potential responses at 50 mV/s scan rate for bare CD-R gold substrates and modified substrates ($\text{Au-S(CH}_2\text{)}_{11}\text{OH}$), respectively. A 1.0 mM solution of Fe(CN)_6^{3-} was used as the electroactive species with 0.1 M KCl as the supporting electrolyte. The cyclic voltammogram (CV) of bare gold substrates presented an expected shape, that is, two clear-cut and symmetric peaks representing the reduction of Fe(CN)_6^{3-} to Fe(CN)_6^{4-} and reoxidation of Fe(CN)_6^{4-} . It showed the chemical reversibility ($i_p^a = i_p^c$) and the $t^{-1/2}$ decay of the current beyond the maximum, which is characteristic of a diffusion-limited (electrochemically reversible) one-electron redox process.⁴⁵ When compared with the voltammetric behavior on bare gold substrates, there were dramatic changes after the gold substrates were modified with the SAMs. The currents are much lower, as compared to those of bare gold substrates, and most of the current is capacitive. This is well-understood as a result of the decreased interfacial electron transfer rate when electrodes are modified with closely packed organic monolayers.^{46,47} The direct comparison of the CVs in Figure 1b confirmed the ideality of the gold electrodes from CD-Rs and the quality of the SAMs formed on CD-R gold substrates despite the fact that the substrates are pregrooved into micrometer features.¹

Zirconia thin films were electrodynamically deposited onto both bare CD-R gold substrates and those modified with SAMs in an aqueous electrolyte of 5.0 mM ZrOCl_2 and 0.1 M KCl by cycling the potential between -1.1 V and $+0.7 \text{ V}$ (vs. Ag|AgCl) for 10 consecutive scans at a scan rate of 20 mV/s (unless otherwise stated). Figure 2 illustrates the comparison between the voltammetric responses for the formation processes as well as the morphological features of thus formed zirconia thin films on bare and modified CD-R gold substrates. In Figure 2a, the dashed line represents the first and last of the 10 scans that were performed on bare CD-R gold substrates, and the solid line shows the behavior on $\text{Au-S(CH}_2\text{)}_{11}\text{OH}$. Although the general features of these CVs are quite similar in terms of the current and peak positions, the CVs on the CD-R gold substrates modified with SAMs showed significant suppression of the oxygen reduction that was observed from -0.1 V to -0.6 V (vs Ag|AgCl). The irreversible peaks around -0.95 V and -1.05 V (vs Ag|AgCl) that are believed to correspond to the complex redox behavior of

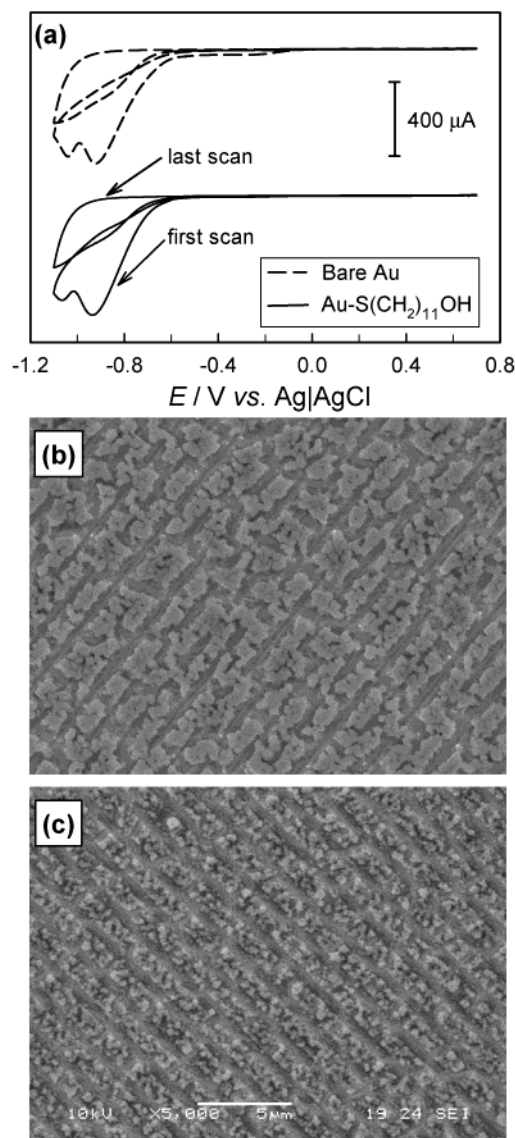


Figure 2. (a) Cyclic voltammograms for bare gold substrates from CD-Rs (---) and $\text{Au-S(CH}_2\text{)}_{11}\text{OH}$ (—) in 5.0 mM ZrOCl_2 and 0.1 M KCl aqueous solution at a scan rate of 20 mV/s ; (b, c) SEM images of zirconia thin films formed on bare CD-R gold substrates and on $\text{Au-S(CH}_2\text{)}_{11}\text{OH}$, respectively. The accelerating voltage of the electron beam used was 10 kV , and the magnification setting used for imaging was $\times 5000$.

ZrOCl_2 on gold^{39–42} were slightly negatively shifted on the modified surfaces as a result of the presence of the blocking SAMs on the electrode surface.^{46,47} However, a significant decrease of the cathodic current on $\text{Au-S(CH}_2\text{)}_{11}\text{OH}$ was not observed, as compared with that on bare gold in this case, possibly because of the very negative potential window and the partial desorption of the monolayers.^{48–51} It should be noted that each run of the 10 cycles became more and more attenuated (i.e., reduction peaks became less pronounced and peak currents decreased). This is clearly shown by the significant difference between the first and

(45) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*, 2nd ed.; John Wiley & Sons: New York, 2001.
 (46) Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1987**, *109*, 3559.
 (47) Finklea, H. O. *Electroanal. Chem.* **1996**, *19*, 109, and references therein.

(48) Walczak, M. W.; Popenoe, D. D.; Deinhammer, R. S.; Lamp, B. D.; Chung, C.; Porter, M. D. *Langmuir* **1991**, *7*, 2687.
 (49) Schneider, T. W.; Buttry, D. A. *J. Am. Chem. Soc.* **1993**, *115*, 12391.
 (50) Yang, D. F.; Wilde, C. P.; Morin, M. *Langmuir* **1997**, *13*, 243.
 (51) Beulen, M. W. J.; Kastenbergh, M. I.; van Veggel, F. C. J. M.; Reinhoudt, D. N. *Langmuir* **1998**, *14*, 7463.

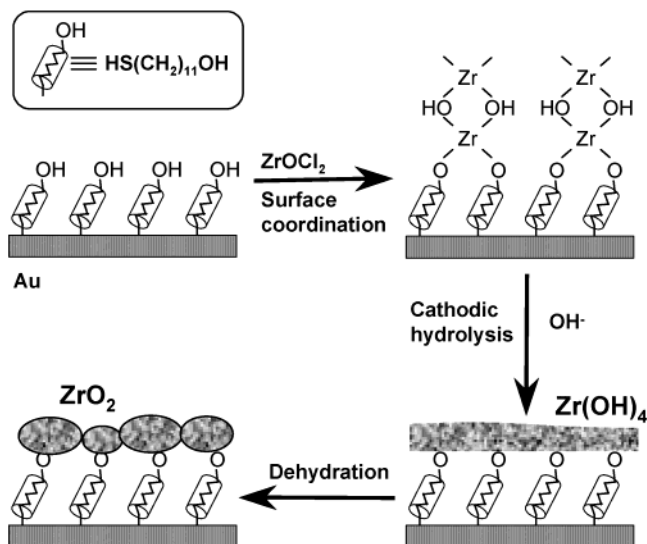


Figure 3. Schematic illustration of the formation of zirconia thin films and the proposed reaction pathway.

last scans of the CVs in Figure 2a. The decrease of the cathodic current can be understood by considering the continual build up of zirconia thin films, which consequently generate higher resistance for the redox processes. The most pronounced and intriguing finding was observed via the comparison between the SEM images of thus formed zirconia thin films on these CD-R gold substrates. As can be seen from Figure 2b and c, zirconia thin films were selectively deposited onto different areas of the substrate, that is, preferential growth of the zirconia islands (particles) along the “mountains”. The zirconia thin film on CD-R gold substrates functionalized with SAMs shows much better confinement to the mountains, as well as more uniform and smaller particle size as compared to those on bare gold substrates.

It has been a challenge to understand the exact mechanism for electrodeposition of zirconia thin films, particularly on organic-modified substrate surfaces.^{39–42} In retrospect, the effective utilization of SAMs for solid state and biomimetic synthesis has inspired continued efforts to fabricate organized inorganic thin films on metal or semiconductors.^{15–17,20,21,43,44,52} For example, methyl- and sulfonate-terminated SAMs on SiO₂/Si were used in the aqueous phase synthesis of ZrO₂ thin films,^{43,44} and dithiolated SAMs on gold were utilized to promote the growth of microcrystalline ZrO₂.^{41,42} On the basis of these initial studies^{13–16} and our present observations, a hypothetical mechanism for the electrochemical deposition of zirconia thin films on CD-R gold substrates modified with hydroxyl-terminated SAMs was proposed and is schematically displayed in Figure 3. Similar to the surface coordination reaction between titanium alkoxides to hydroxyl terminated SAMs on gold,⁵³ ZrOCl₂ molecules are attached to the OH-terminated monolayers via a ligand exchange reaction of the SAM's terminal alcohols with chloride ligands (Figure 3). The formation of hydroxyl-terminated monolayers on gold and the further coordination of zirconium were also confirmed by both wetting measurements and preliminary SEM/EDX results.⁵⁴ The following cathodic hydrolysis (i.e., the generation of OH[−] species from H₂O and O₂

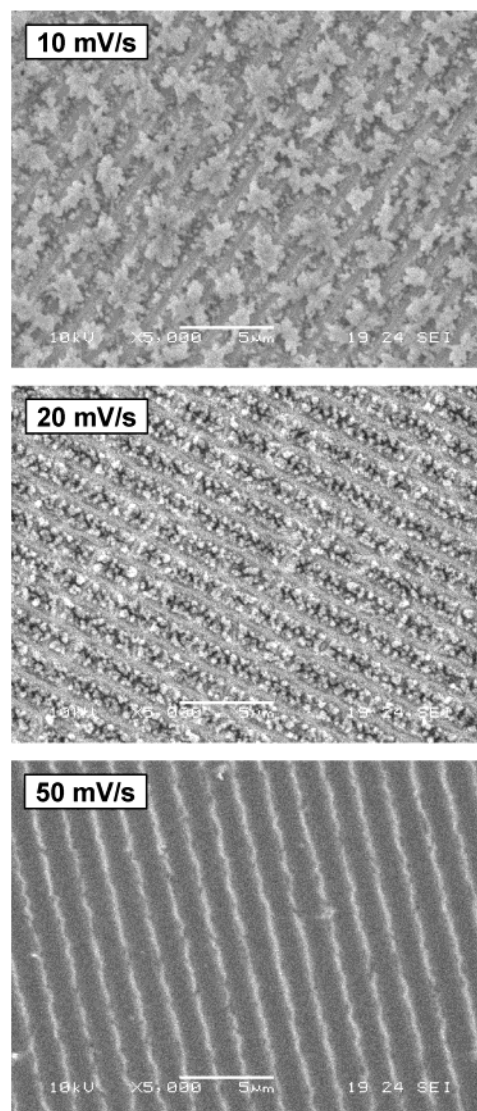


Figure 4. SEM images of zirconia thin films formed on Au–S(CH₂)₁₁OH. Samples were prepared by voltammetric cycling at different scan rates under experimental conditions otherwise identical to those in Figure 2.

to hydrolyze the surface-coordinated zirconium) to produce Zr(OH)₄ and the dehydration to finally form ZrO₂ particle/thin films were recommended previously.^{39–42} Further discussion and investigation are deserved to clarify the very details of this mechanism but are beyond the scope of this report. In addition, it is more practically imperative yet remarkably interesting to pursue the possible dynamic control of the formation of differently featured zirconia thin films.

To direct our efforts, zirconia thin films were deposited onto Au–S(CH₂)₁₁OH surfaces at scan rates of 50, 20, and 10 mV/s under otherwise identical aforementioned experimental conditions. As shown in Figure 4, significant differences in surface coverage, nucleation, and particle growth were present. At a scan rate of 50

(52) Brinker, C. J. *Curr. Opin. Colloid Interface Sci.* **1998**, *3*, 166.

(53) Banks, J. T.; Yu, T. T.; Yu, H. Z. *J. Phys. Chem. B* **2002**, *106*, 3538.

(54) The presence of 11-mercaptopundecanol SAMs on gold (Au–S(CH₂)₁₁OH) was also verified by wetting measurements.⁵³ Scanning electron microscopy (SEM) of the samples in conjunction with an energy-dispersive X-ray (EDX) detector revealed the presence of zirconium by Zr-Kα and Zr-Kβ peaks after the electrochemical scanning in 5.0 mM ZrOCl₂·8H₂O and 0.1 M KCl.

mV/s, the sample had an almost uniform film formation on the mountains of the CD-Rs' track trails, with less pronounced formation in the valleys. The sample at 20 mV/s was very different; it yielded distinct ZrO_2 particle (islands) formation only on the mountains of the substrate. The particles formed were in the range of a few hundred nanometers and maintained uniform alignment along the mountains of the CD-R gold substrate to form oriented zirconia "microstrips". The particles were of different shapes, and their placement appeared largely random in the strips. Finally, the sample cycled at 10 mV/s showed another type of formation of zirconia thin films: it possessed a much larger, amorphous, cluster-like growth and nucleation on top of or spawning from the smaller particles without clear confinement to the mountains. In addition, prolonged voltammetric scanning or constant-potential polarization would result in a coating film having a "cracked-mud" appearance (Figures not shown),⁴⁰ irrespective of the substrate features. The unique dependence of the morphological features of zirconia thin films prepared by electrodeposition on the potential scan rate suggests a strong correlation between local concentration of cathodically produced bases (OH^-) and the micrometer mountain–valley surface profile of the substrate, although a detailed explanation is not imminent at this stage. It is well-known that cathodic electrodeposition is governed by Faraday's law, and the amount of deposited materials can be controlled by varying the deposition time or current density.⁵⁵ The selective growth of zirconia thin films on mountains at an optimized scan rate might be understood by the role of the ionic depletion in the valleys, as well as the preferred coagulation of ZrO_2 particles on the mountains that are enhanced by the stronger electric field along the edges.^{55,56} Nevertheless, as a unique example, this observation explores the potential of using simple electrochemical control to tune the formation and feature of inorganic material microstructures.

Zirconia thin films were also prepared on CD-R gold substrates modified with differently functionalized SAMs (i.e., with different terminal groups, such as $-\text{COOH}$, $-\text{OH}$, and $-\text{CH}_3$) under otherwise identical experimental conditions. This was done in order to give further insights into the possible effects of surface functionalization on the formation of inorganic thin films on prepatterned substrates. Such an effort stems from both the evident difference between zirconia thin films formed on bare gold substrates and those modified with hydroxyl-terminated SAMs (Figure 2), as well as the recent studies of the deposition of metal oxide thin films on differently functionalized SAMs.^{15–21} As evident from Figure 5, zirconia thin films formed on $-\text{COOH}$, $-\text{OH}$, and $-\text{CH}_3$ -terminated SAMs show significant differences among each other. The $\text{Au}-\text{S}(\text{CH}_2)_{10}\text{COOH}$ sample retained some individual shape and character, as compared to the distinct particle features on the $\text{Au}-\text{S}(\text{CH}_2)_{11}\text{OH}$; the ZrO_2 particles were much more integrated and exhibited extensive amalgamation on the mountain and even some part of the valley regions of the track trails. Zirconia thin films formed on $\text{Au}-\text{S}(\text{CH}_2)_{11}\text{CH}_3$ were devoid of any specific island formation, yielding almost "transparent" uniform layers (i.e., to the SEM, as the CD-R track trails were easily observed beneath the film) that spanned across the track trails. In addition, the uniform zirconia thin film thus formed had

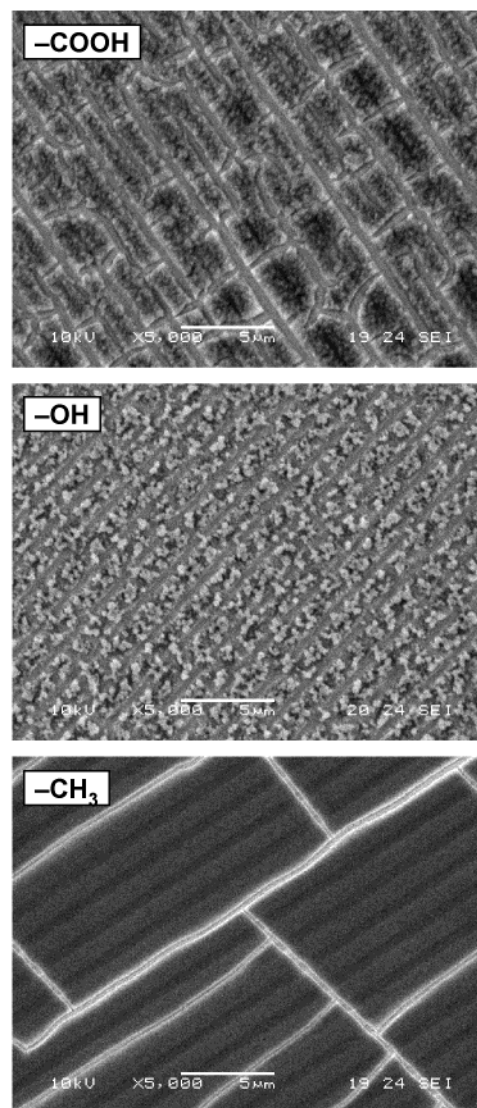


Figure 5. SEM images of zirconia thin films prepared on differently functionalized CD-R gold substrates (i.e., $\text{Au}-\text{S}(\text{CH}_2)_{10}\text{COOH}$, $\text{Au}-\text{S}(\text{CH}_2)_{11}\text{OH}$, and $\text{Au}-\text{S}(\text{CH}_2)_{11}\text{CH}_3$). All samples were prepared and imaged under experimental conditions otherwise identical to those in Figure 2.

orderly groove-directed "cracks" that might have occurred as a result of the drying (or dehydration) of the films.⁴⁰

As mentioned above, the formation of uniform and fine-patterned zirconia thin films consisting of distinct submicrometer particles on hydroxyl terminated SAMs can be understood by the effect of the surface coordination reactions between the zirconium species in the solution to the surface hydroxyl groups.^{41,42} With carboxyl and methyl SAMs, we believe that interactions between the solution species and SAMs contribute quite differently to the film formation. In the case of the carboxyl group, the possible surface charge (which is sensitive to the local pH) will further contribute to the formation of the films. This is consistent with other reports utilizing acidic groups.^{15–17,20,21,43,44} For the methyl-terminated surface, the selective nucleation and growth of ZrO_2 particles are not favored because of the uniform and hydrophobic surface properties. The preliminary X-ray diffraction (XRD) studies showed the amorphous nature of these zirconia thin films, despite the selection of substrates and electrochemical scan rates,⁵⁷ which

(55) Zhitomirsky, I.; Gal-Or, L. In *Intermetallic and Ceramic Coatings*; Dahotre, N. B., Sudarshan, T. S., Ed.; Marcel Dekker: New York, 1999.

(56) De, D.; Nicholson, P. S. *J. Am. Ceram. Soc.* **1999**, *82*, 3031.

is seemingly different from the microcrystalline formation at a much faster scan rate (200 mV/s) on "flat" gold substrates.^{41,42}

It should be noted that these simple, conductive, and micro-patterned CD-R gold substrates do not have varied features and resolutions for the fabrication of complex microstructures,⁵⁸ but it should be very suitable for many applications in chemistry, biology, and materials science, particularly for the study of selective crystal growth, template-directed deposition of inorganic thin films, and biomimetic synthesis on surfaces. In addition, the present approach deserves further discussion and investigation regarding the microscopic mechanism of electrodeposition on patterned substrates as well as the correlation between the surface functionalization and the formation of differently featured thin films.

CONCLUSIONS

In summary, we have demonstrated a practical method of using CD-R gold as a simple, inexpensive, and micropatterned conductive substrate for the fabrication of material microstructures. In particular, CD-R gold substrates with pregrooved micropatterns can be successfully used for templated electrodeposition of

zirconia thin films. The present results also indicate that functional groups of the selected monolayer allow for unique zirconia thin film formation based on specific deposition conditions via electrochemistry (i.e., a tailored scan rate and cycle number that yields reproducible thin film formation features). The variation of the functional groups of the selected SAMs combined with electrodynamic control to "customize" the formation of functional inorganic thin films holds promise for technological applications.

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(57) Preliminary X-ray diffraction analysis of the films was performed at room temperature using a Rigaku (D/max-RAPID) X-ray diffractometer at 46 kV and 42 mA with a filtered Cu-K α line. Peaks due to the underlying gold substrate were clearly observed, but no zirconia peaks were evident.

(58) Deng, T.; Wu, H. K.; Brittain, S. T.; Whitesides, G. M. *Anal. Chem.* **2000**, *72*, 3176.