

Dendrimer-Mediated Adhesion between Vapor-Deposited Au and Glass or Si Wafers

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Here, we report the use of amine-terminated poly(amidoamine) (PAMAM) dendrimers as adhesion promoters between vapor-deposited Au films and Si-based substrates. This method is relatively simple, requiring only substrate cleaning, dipping, and rinsing. Proof of concept is illustrated by coating glass slides and single-crystal Si wafers with monolayers of PAMAM dendrimers and then evaporating adherent, 150-nm-thick Au films atop the dendritic adhesion promoter. Scanning tunneling microscopy and cyclic voltammetry have been used to assess the surface roughness and electrochemical stability of the Au films. The effectiveness of the dendrimer adhesion layer is demonstrated using standard adhesive-tape peel tests.

We describe the use of amine-terminated poly(amidoamine) (PAMAM) dendrimers^{1,2} as adhesion promoters between oxidized Si surfaces (denoted here as SiO_x) and Au thin films deposited by physical vapor deposition (PVD). Although interactions between single primary amine groups and both Au³ and SiO_x⁴ are relatively weak, high-generation PAMAM dendrimers have tens or hundreds of terminal primary amine groups per molecule, and it is the aggregate strength of these multidentate interactions with inorganic substrates that renders dendrimers suitable for enhancing adhesion between materials that are otherwise prone to delamination.

Many methods have been developed for enhancing adhesion between intrinsically nonadherent materials. Here we focus on the ubiquitous SiO_x/Au adhesion problem. Depending on the specific application, adhesion between these materials can be promoted using interlayers of metals such as Cr or Ti,⁵ ion beam bombardment,^{6,7} or bifunctional organic molecules or polymers.^{8–13}

Cr and Ti adhesion layers migrate along grain boundaries^{14–16} and therefore result in the formation of intermetallics that compromise the electrical, photonic, and chemical properties of both Au and Si. Deposition at elevated temperature, which is often desirable or unavoidable, exacerbates this problem. Interdiffusion can be largely eliminated by use of a second metal that acts as a diffusion barrier for the first. In the case of Cr and Ti adhesion layers, Pd and Pt can act as diffusion barrier layers but this requires the deposition of three metals which may introduce more complexity than is feasible for many applications.^{14,17} Ion beam techniques can be technically challenging and may result in poor adhesion.

Organic adhesion layers are useful for applications requiring ultrathin metal layers (by eliminating the need for a metallic adhesion layer),^{18,19} and they also eliminate the possibility of metal interdiffusion. However, organic adhesion promoters, especially those based on monolayers, are notoriously difficult to prepare and often result in defective regions in the metal overlayer. Mercaptosilane monolayers^{8,10,12,19} are among the most well-known organic adhesion layers for SiO_x/Au. However, the silanes tend to polymerize, which leads to defects and irreproducible adhesion, and the Si substrates usually require significant pretreatment. Previous studies examining the use of amine-terminated self-assembled monolayers (SAMs) as adhesion promoters have met with limited success.²⁰ In contrast, organic adhesion layers composed of dendrimers benefit from a relatively simple preparation method involving only careful substrate cleaning, dipping, and rinsing. Moreover, the necessary dendritic materials are commercially available. Adsorption of dendrimers to many materials, some relevant to this report, has been previously described in the literature. For example, adsorption of dendrimers to Si-

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- (1) Tomalia, D. A.; Naylor, A. M.; Goddard, W. A. *Angew. Chem., Int. Ed. Engl.* **1990**, 29, 138–175.
- (2) Zeng, F.; Zimmerman, S. C. *Chem. Rev.* **1997**, 97, 1681–1713.
- (3) Xu, C.; Sun, L.; Kempley, L. J.; Crooks, R. M.; Ricco, A. J. *Anal. Chem.* **1993**, 65, 2101–2107.
- (4) Lee, Y. *Langmuir* **1999**, 15, 1796–1801.
- (5) Holloway, P. H. *Gold Bull.* **1978**, 12, 99–106.
- (6) Mitchell, I. V.; Williams, J. S.; Smith, P.; Elliman, R. G. *Appl. Phys. Lett.* **1984**, 44, 193–195.
- (7) Jang, H. G.; Kim, K. H.; Han, S.; Choi, W. K.; Jung, H.-J.; Koh, S. K.; Kim, H. B. *J. Vac. Sci. Technol. A* **1997**, 15, 2234–2237.
- (8) Wasserman, S. R.; Biebuyck, H.; Whitesides, G. M. *J. Mater. Res.* **1989**, 4, 886–892.
- (9) Mumbauer, P. D.; Carey, D. H.; Ferguson, G. S. *Chem. Mater.* **1995**, 7, 1303–1314.

- (10) Chaudhury, M. K.; Plueddemann, E. P. *J. Adhes. Sci. Technol.* **1987**, 1, 243–246.
- (11) Czanderna, A. W.; King, D. E.; Spaulding, D. J. *Vac. Sci. Technol. A* **1991**, 9, 2607–2613.
- (12) Newton, M. I.; McHale, G.; Hooper, P. D.; Willis, M. R.; Burt, S. D. *Vacuum* **1995**, 46, 315–318.
- (13) Smith, E. L.; Alves, C. A.; Anderegg, J. W.; Porter, M. D.; Siperko, L. M. *Langmuir* **1992**, 8, 2702–2714.
- (14) Tisone, T. C.; Drobek, J. *J. Vac. Sci. Technol.* **1971**, 9, 271–275.
- (15) Ashwell, G. W. B.; Heckingbottom, R. *J. Electrochem. Soc.* **1981**, 128, 649–654.
- (16) Adzic, R.; Horkans, J.; Cahan, B. D.; Yeager, E. J. *Electrochem. Soc.* **1973**, 120, 1219–1220.
- (17) Josowicz, M.; Janata, J.; Levy, M. *J. Electrochem. Soc.* **1988**, 135, 112–115.
- (18) Kim, T.; Chan, K. C.; Crooks, R. M. *J. Am. Chem. Soc.* **1997**, 119, 189–193.
- (19) Goss, C. A.; Charych, D. H.; Majda, M. *Anal. Chem.* **1991**, 63, 85–88.
- (20) Dunaway, D. J.; McCarley, R. L. *Langmuir* **1994**, 10, 3598–3606.

based surfaces, in the form of glass slides and silica particles,^{21,22} and adsorption of dendrimers to Au surfaces²³ and colloids²⁴ have been studied. The use of dendrimers to bind submonolayers of colloidal Au particles to Si has also been reported.²⁵

EXPERIMENTAL SECTION

Chemicals. The following chemicals and materials were used as received; H₂SO₄ (concentrated, EM Science), H₂O₂ (30%, J. T. Baker), HF (48%, EM Science), HClO₄ (70%, Fisher), KCl (99.99%, Aldrich), Ru(NH₃)₆Cl₃ (Strem Chemicals), Micro-90 cleaning solution (VWR Scientific), microscope slides (ESCO), Si(100) wafers (Transition Technology International), Starburst PAMAM dendrimers (Dendritech, Inc., Midland, MI), and punctilious ethanol (Quantum). Peel tests were performed using Scotch Magic Tape No. 810 (3M). Evaporated Au was derived from a Canadian Maple Leaf Au coin (99.99%, Canadian Mint). HS(CH₂)₁₅CH₃ (C16SH) (92%, Aldrich) was distilled once prior to use.

Characterization. FT-IR-external reflection spectroscopy (FT-IR-ERS) measurements were made using a Digilab FTS-40 spectrometer equipped with a Harrick Scientific Seagull reflection accessory and a liquid N₂-cooled MCT detector.²³ All spectra were the sum of 512 or fewer scans using *p*-polarized light at an 84° angle of incidence with respect to the Au substrate normal. Electrochemical measurements were made using a Pine Instruments AFRDE4 bipotentiostat equipped with a Kipp & Zonen X–Y recorder. A three-electrode configuration was used consisting of a Pt gauze counter electrode, a Ag/AgCl, 3 M NaCl reference electrode (Bioanalytical Systems, West Lafayette, IN), and a 0.33-cm² vapor-deposited Au working electrode. Scanning tunneling microscopy (STM) data were acquired in air in the constant-current mode using a Nanoscope III STM (Digital Instruments, Santa Barbara, CA). The tips were mechanically cut 80/20 Pt/Ir (Digital Instruments). A bias of 300 mV and a tunneling current of 150 pA were used to obtain all data. The *z*-scale and root-mean-square (rms) roughness for each image are noted in the figure captions. Prior to analysis, Au substrates were cleaned using an ozone cleaner (Boekel Industries, Inc., model 135500).

Substrate Preparation. Substrate preparation and cleanliness are of critical importance in this experiment. Glass microscope slides were cleaned prior to use by soaking overnight in 2% Micro-90 cleaning solutions to remove particulate material from the surface. After thorough rinsing with deionized water, the slides were placed in freshly prepared piranha solution (3:1 H₂SO₄/30% H₂O₂) for 1 h to remove organic impurities. (**Caution:** piranha solution is a powerful oxidizing agent and reacts violently with organic compounds. It should be discarded immediately after use in a waste container with a loose-fitting cap). The slides were then rinsed thoroughly with deionized water and transferred to beakers of ethanol. Si wafers were etched in HF for 20 min, rinsed with deionized water, and then cleaned following the just-described

procedure for the glass microscope slides. Substrates were then soaked in 1 μM ethanolic solutions of the PAMAM dendrimers for 3 h, removed from solution, rinsed copiously with ethanol, and then dried in a stream of flowing N₂. Au depositions were carried out using a modified Varian model 3117 Vacuum Coating System (TFS Technologies, Albuquerque, NM). The deposition rate was ~0.2 nm/s and the base pressure was 10⁻⁵ mmHg. The final thickness of the Au overlayer was ~150 nm.

RESULTS AND DISCUSSION

Peel testing is a qualitative method that is often used to assess the strength of adhesion between thin films and substrates.⁸ In this test, adhesive tape is firmly pressed into contact with a metal overlayer and then peeled off at a constant rate. The amount of metal transferred to the tape is a measure of the adhesive strength of the film. In the absence of an adhesion layer, vapor-deposited Au is always easily removed from Si-based substrates by peeling.

We used peel testing to evaluate the effectiveness of G2, G4, G6, and G8 PAMAM-dendrimer adhesion layers. The G8 adhesion layer afforded the best results, most likely due to the high density of amine groups per unit area achieved at the densely packed surface of the dendrimer. For example, G8 has a total of 1024 primary amine groups per dendrimer, which corresponds to a primary amine surface density of 3.5 amines/nm². Films prepared with G2, G4, or G6 tended to exhibit weaker adhesion and gave less reproducible results.

Good adhesion promotion by the G8 interlayer depends strongly on the cleanliness of the Si substrate. Substandard cleaning prior to dendrimer adsorption resulted in adhesive failure at small defect sites. On properly cleaned substrates having a G8 adhesion layer, however, ~85% of the deposited films that we tested adhered completely to the glass slides when the tape was pressed firmly to the surface and then pulled back at a constant rate of ~0.5 cm/s with the leading edge of the tape parallel to the substrate surface. On substrates that passed this test, a second peel test with the tape pulled off perpendicular to the surface resulted in little to no additional failure. Most films could be forced to fail if the tape was repeatedly applied and removed at a very rapid rate. Occasionally films could not be removed with tape at any peel rate or angle.

Representative 1 μm × 1 μm STM images of Au thin films deposited onto different surfaces are shown in Figure 1. The top and middle images correspond to a 150-nm-thick, vacuum-evaporated Au films on naked and G8-modified Si wafers, respectively. Although the average Au grain size of the film having the G8 interlayer is slightly smaller than the Au film evaporated onto naked Si, the presence of the dendrimer adhesion layer has no significant impact on the Au nanostructure. For example, the rms roughness values measured for the two Au films (Si/Au, 3.3 nm; Si/G8/Au, 3.6 nm) are about the same. Note that neither of these films was thermally annealed. Thermal annealing of Au films²⁶ having a dendrimer adhesion layer using an H₂/O₂ flame leads to adhesion failure, presumably because of the thermally driven retro-Michael addition decomposition pathway for PAMAM dendrimers.²⁷

(21) Tsukruk, V. V.; Rinderspacher, F.; Bliznyuk, V. N. *Langmuir* **1997**, *13*, 2171–2176.

(22) Esumi, K.; Gojino, M. *Langmuir* **1998**, *14*, 4466–4470.

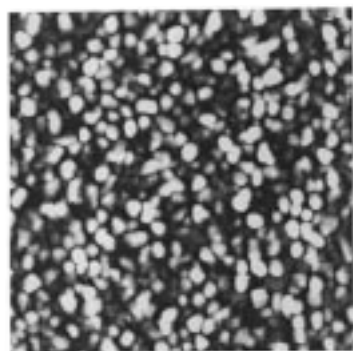
(23) Tokuhisa, H.; Zhao, M.; Baker, L. A.; Phan, V. T.; Dermody, D. L.; Garcia, M. E.; Peez, R. F.; Crooks, R. M.; Mayer, T. M. *J. Am. Chem. Soc.* **1998**, *120*, 4492–4501.

(24) Garcia, M. E.; Baker, L. A.; Crooks, R. M. *Anal. Chem.* **1998**, *71*, 256–258.

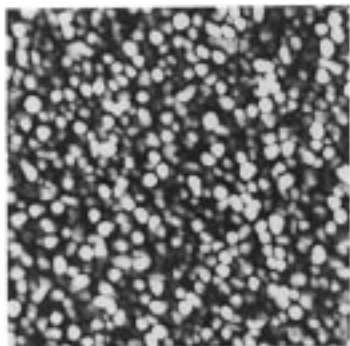
(25) Bar, G.; Rubin, S.; Cutts, R. W.; Taylor, T. N.; Zawodzinski, T. A. *Langmuir* **1996**, *12*, 1172–1179.

(26) Dishner, M. H.; Ivey, M. M.; Gorer, S.; Hemminger, J. C.; Feher, F. J. *J. Vac. Sci. Technol., A* **1998**, *16*, 3295–3300.

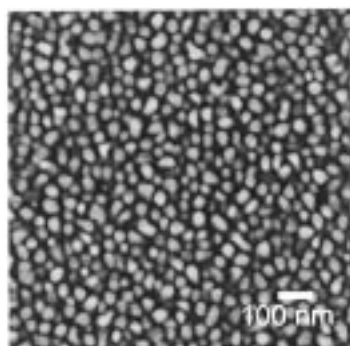
(27) Zhao, M.; Lui, Y.; Crooks, R. M.; Bergbreiter, D. E. *J. Am. Chem. Soc.* **1999**, *121*, 923–930.



Si/Au



Si/G8/Au



Si/Ti/Au

0 15 30
z scale (nm)

Figure 1. Scanning tunneling microscopy images ($1\ \mu\text{m} \times 1\ \mu\text{m}$) of vacuum-evaporated Au films on Si(100) wafers: (top) 150-nm-thick Au film with no adhesion layer (Si/Au); (middle) 150-nm-thick Au film with a G8 PAMAM dendrimer adhesion layer (Si/G8/Au); (bottom) 200-nm-thick Au film having a 20 nm Ti adhesion layer (Si/Ti/Au). The rms roughness values for these three films are 3.3, 3.6, and 2.3 nm, respectively.

For comparison, the bottom image of Figure 1 shows the topography of a 200-nm-thick Au film electron beam deposited onto a Si wafer precoated with a 20-nm-thick Ti adhesion layer. Such substrates are commonly used for testing functional organic thin films. The rms roughness is somewhat smaller than for the other two surfaces shown in Figure 1 (2.3 nm), but otherwise the appearances of all three Au films are rather similar.

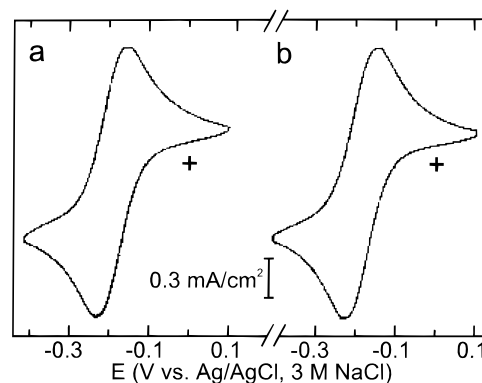


Figure 2. Cyclic voltammetry of aqueous 5 mM $\text{Ru}(\text{NH}_3)_6^{3+}$ at a glass/G8/Au electrode: (a) fifth scan; (b) after 4 h of continuous scanning. Supporting electrolyte, 1 M KCl; scan rate, 0.1 V/s. Cathodic currents are down.

Au films deposited on glass microscope slides having no adhesion layer often lift off when immersed in or rinsed with solvents. This is a consequence of solvent-induced delamination beginning at exposed edges of the substrate. G8 dendrimer adhesion layers prevented such delamination after exposure of the substrates to water (pH 5.5), chloroform, and ethanol for up to 12 h, at which time the tests were discontinued. Films soaked in dilute acids (0.1 M HClO_4) for short times (~ 1 h) also generally resisted delamination. However, soaking in dilute or concentrated aqueous KOH, or concentrated aqueous HCl, resulted in adhesive failure.

Further tests were performed to assess the suitability of dendrimer/Au films for use as electrodes for electrochemical experiments and as platforms for studying SAMs. For example, glass/G8/Au films were electrochemically cycled continuously for 4 h between +0.1 and -0.4 V in aqueous 5 mM $\text{Ru}(\text{NH}_3)_6^{3+}$ (Figure 2). Part a of Figure 2 shows the fifth voltammogram and part b shows the voltammetry after 4 h. There is essentially no change in the shape, peak current ($i_{p,c} = 1.12\ \text{mA}/\text{cm}^2$), or peak splitting ($\Delta E_p = 80\ \text{mV}$) of these voltammograms.

Another important application of vacuum-evaporated Au films is their use as substrates for studying SAMs composed of organomercaptan molecules. Figure 3 shows a reflection infrared spectrum of an *n*-hexadecanethiol (C16SH) SAM confined to a Si/G8/Au substrate (the CO_2 region between 2250 and $2400\ \text{cm}^{-1}$ has been digitally flattened). The peak frequencies (see inset) for the methyl and methylene modes are consistent with literature reports for well-ordered monolayers of C16SH.²⁸ These data indicate that the microstructure of the dendrimer-supported film does not affect the ordering of molecular adsorbates.

SUMMARY AND CONCLUSIONS

We have described a new approach for preparing adherent Au thin films on glass and Si surfaces. Although lower generation PAMAM dendrimers could be effective adhesion promoters, we found that the best adhesion was obtained from the G8 dendrimer. Because the total surface coverage of dendrimers is largely independent of generation,²³ we conclude that the interaction between the dendrimer and the substrate and the Au film is

(28) Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1987**, *109*, 3559–3568.

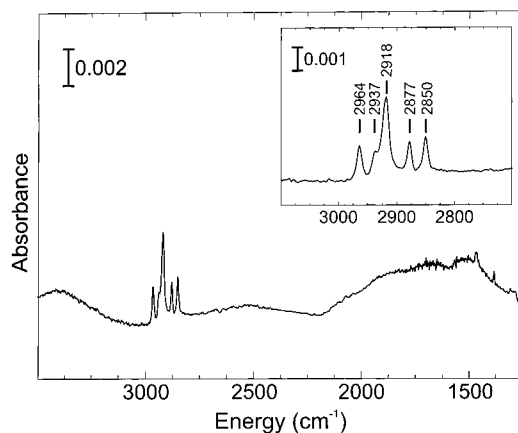


Figure 3. FT-IR-ERS of an *n*-hexadecanethiol (C16SH) self-assembled onto a Si/G8/Au surface. The CO₂ region between 2250 and 2400 cm⁻¹ has been digitally flattened, but no additional baseline correction was applied.

maximized for the highest level of multidentate interactions. On the basis of previous results in which we showed that even low-generation dendrimers formed adherent layers on Au substrates, we conclude that the substrate (Si/dendrimer or glass/dendrimer) interaction is weaker than the dendrimer/Au interaction. This is

also consistent with our finding that the Si and glass substrates must be very clean for optimal adhesion.

Our results show that dendrimer-based adhesion is inferior to that obtained using very carefully prepared mercaptosilane adhesion layers,¹⁹ but the approach described here is simpler and more reproducible and the results are acceptable for many common applications. For example, dendrimer-mediated adhesion was shown to be suitable for preparing and studying self-assembled monolayers and for electrochemical studies in aqueous solvents at neutral pH. We expect that dendrimers will act as good adhesion layers for many other applications, as they interact strongly with many other metals and semiconductors.

ACKNOWLEDGMENT

We gratefully acknowledge the National Science Foundation (Grant CHE-9818302) and the Robert A. Welch Foundation for support of this research. We also thank Mr. Mark Kaiser (Dendritech, Inc., Midland, MI) for providing technical information and the Starburst PAMAM dendrimers used in this study.

Received for review May 11, 1999. Accepted June 29, 1999.

AC990495E