Healing of Defects in the Stepwise Formation of Polymer/Silicate Multilayer Films

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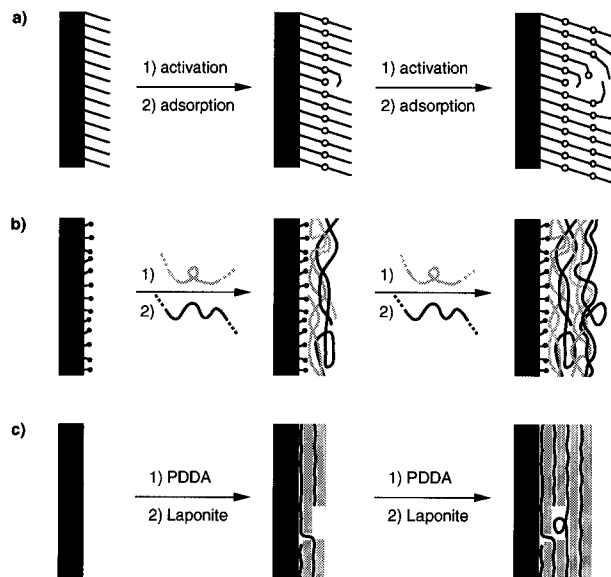*Department of Chemistry, Lehigh University
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Nanostructured solids are of interest in many fields,[1] including optics,[2] molecular sensing,[3] and microelectronics.[4] In particular, thin films built by the adsorption or deposition of individual layers have great potential due to their precisely controllable thickness and variable molecular structure. In recent years, synthetic strategies have been developed for the formation of multilayered structures[5–8] using self-assembled monolayers (SAMs)[9] as components. Formation of SAMs relies upon chemisorption of individual molecules to a substrate surface, and multilayers may be formed by alternating the adsorption of a SAM with activation of the new surface to create the next generation of adsorption sites. For this approach to be successful in creating an ordered structure (one with a regular modulation of composition in the direction normal to the substrate), a constant, or nearly constant, number of active sites must be maintained at the surface as each layer is added. If sites are lost (e.g., molecules fail to react) in any particular cycle, the resulting defects may be propagated into subsequent layers (Figure 1a).[10] The resulting disorder may be evidenced, for example, by the absence of distinct Bragg peaks in the film's X-ray diffraction (XRD) pattern.[11] A strategy that overcomes the potential for loss of sites is the alternate adsorption of oppositely charged polyelectrolytes,[12,13] though interpenetration of the components in adjacent layers[14] (Figure 1b) limits the structural order attainable in such systems.

We recently reported a new method for the formation of nanostructural multilayers via alternate adsorption

Figure 1. Schematic illustrations of (a) the formation and propagation of a defect in a multilayered film prepared by the alternate self-assembly and activation of molecular adsorbates, (b) the formation of a film by the alternate adsorption of oppositely charged polyelectrolytes onto a pretreated substrate, and (c) the formation and "healing" of a microscopic defect in a film prepared by the alternate adsorption of PDDA and Laponite onto bare Si/SiO$_2$.

of a cationic polyelectrolyte [poly(diallyldimethylammonium chloride), PDDA] and the anionic sheets of an exfoliated clay (Laponite RD, a synthetic form of hectorite).[15,16] The regular growth and nanometer-scale order of these composite films indicate that the lateral dimensions of the silicate sheets (~25–35 nm) adsorbed in any cycle are sufficiently large not only to prevent interpenetration by the polymer but also to cover, or "heal", packing defects formed in the preceding adsorption cycle (Figure 1c). Hence, presumably, no such defect is permanent, and structural order can be maintained as the films grow in thickness. In this communication, we provide direct evidence for such "healing" by examining the influence of *macroscopic* defects on the growth of PDDA/Laponite multilayered films. These experiments provide insight into the mechanism of formation of such materials and illustrate the important conceptual advance behind incorporating rigid, "two-dimensional" components into multilayered films.[15,16] Our results also have the practical significance of indicating that these films can be grown on a wide variety of substrates, whether or not their surfaces are active with respect to adsorption of either component.

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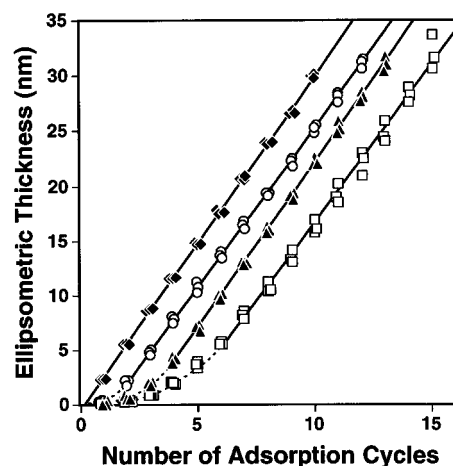
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As model "defects" with which to demonstrate healing, we chose substrates with low surface energy and low affinity for the ionic macromolecules used in the adsorptions: ordered, methyl-terminated SAMs formed by adsorption of octadecyltrichlorosilane (OTS) onto Si/SiO$_2$ and by adsorption of hexadecanethiol (HDT) onto silver.[9,17,18] Substrates were treated alternately with a 5% (w/w) aqueous solution of poly(diallyldimethylammonium chloride) (PDDA, Polysciences) for ~5 s and with a 0.2% (w/w) aqueous suspension of synthetic hectorite (Laponite RD, Laporte Industries, Ltd.) for ~5 s; samples were thoroughly rinsed with purified water (Millipore Milli-Q, 15–17 MΩ cm) and dried with a jet of nitrogen after each step.[15] In no case were the substrates pretreated to promote adhesion of these components; the first step in formation of all films was adsorption of PDDA.

The inertness of the SAMs with respect to adsorption of the two macromolecular precursors was confirmed using optical ellipsometry (Rudolph Auto-EL III): a single sequential treatment with PDDA and then with Laponite produced less than 0.2 nm of growth on top of the SAMs on either substrate.[19] Repeated adsorption cycles, however, led eventually to an average growth in thickness of 2.9 nm/cycle on the SAM on Si/SiO$_2$ and 3.0 nm/cycle on the SAM on Ag, which was nearly identical with the growth seen on bare Si/SiO$_2$ (3.0 nm/cycle). As shown in Figure 2, regular growth began with the fifth cycle on the SAM on Ag and with the seventh cycle on the SAM on Si/SiO$_2$. To confirm that multiple adsorption cycles were necessary—that the entire surface could not be covered in a single cycle using longer adsorption times—we allowed SAMs on Si/SiO$_2$ to soak in the PDDA solution and then in the Laponite suspension for 16 h each. The samples emerged dry from the component solutions and rinse water, with the exception of a few tiny droplets pinned at isolated sites. The total growth in thickness on these samples was less than 0.6 nm, compared to ~5 nm of growth on bare Si/SiO$_2$ substrates that were treated in the same way.

The changes in ellipsometric thickness displayed in Figure 2 were accompanied by qualitative changes in

Figure 2. Ellipsometric growth of multilayers as a function of the number of adsorption cycles on: bare Si/SiO$_2$ (◆); SAMs formed by adsorption of HDT onto Ag (▲) and OTS onto Si/SiO$_2$ (□);[17] and an incomplete SAM formed by adsorption of OTS onto Si/SiO$_2$ (○).[26] Dashed curves are guides for the eye through data *not* included in the least-squares (solid) lines. The data shown in this figure are from individual samples; similar results were seen on other samples.

the wettability of the substrate surfaces. The SAMs were initially hydrophobic,[17] and the reagent solutions and rinse water rolled around easily on their surfaces. Within only two cycles for the SAMs on Ag, however, small spots (<1 mm across) remained wet after application of the reagent solutions and the rinse water, and within six adsorption cycles the entire surface remained wet. The SAMs on Si/SiO$_2$ were more resistant to growth, requiring four cycles before small spots remained wet and seven before the entire surface of the sample remained wet. For comparison, the bare Si/SiO$_2$ surface was hydrophilic and remained so throughout formation of the multilayer.

To confirm that the multilayers were formed on top of the methyl-terminated monolayers and did not displace them from the surface, we performed 17 adsorption cycles on a SAM on Si/SiO$_2$, monitoring the growth ellipsometrically, and then gently swabbed and rinsed the sample with ethanol and water to remove the multilayer structure. Advancing and receding contact angles of water (109–111° and 95–99°) and hexadecane (42–43° and 41–42°) on this surface were similar to those measured prior to adsorption of the multilayer.[17] Furthermore, the ellipsometric thickness of the SAM was 2.5 nm, the same as was measured before adsorption of the multilayer. These results provide strong evidence that the alkylsiloxane monolayer remained intact throughout adsorption of the multilayer.[20]
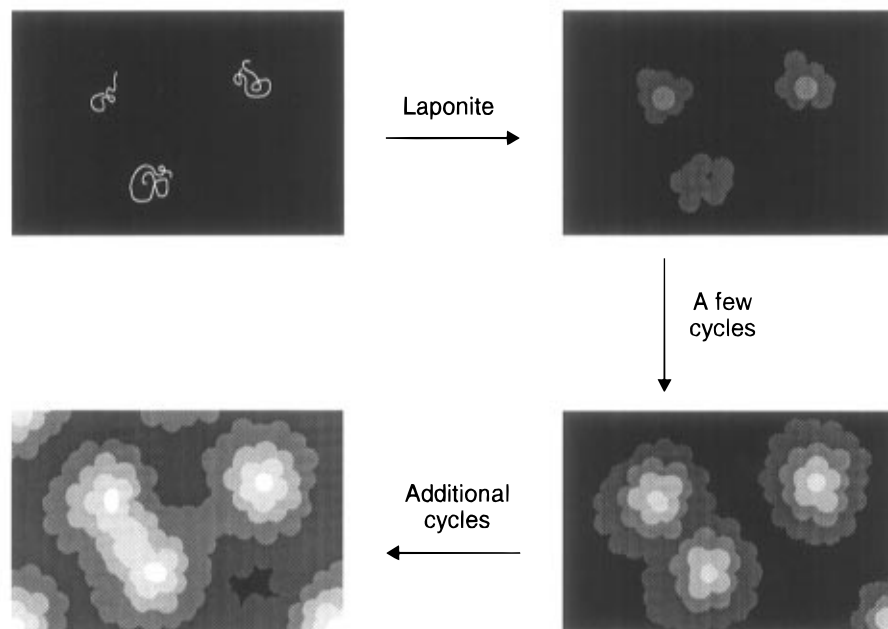
Since PDDA and Laponite each have little or no affinity for the surfaces of the SAMs on either substrate, we infer that multilayer growth begins by adsorption of the polymer at imperfections[21] in the SAM. In any place where the polymer adsorbs, Laponite may then adsorb, forming an island that is ideal for adsorption of more polymer, and then more Laponite, in subsequent steps. As growth of the film progresses, these islands

(17) Substrates for the formation of multilayered films were prepared as follows. Silicon wafers were broken into small pieces (~1 cm × ~2 cm) and cleaned by immersion in a 3:7 (v/v) solution of 30% H$_2$O$_2$ and concentrated H$_2$SO$_4$ (**Caution**: This solution reacts violently with organic materials). To prepare SAMs, these pieces were treated for 5 min in ~9 mM solutions of octadecyltrichlorosilane (OTS, Aldrich) in 80% hexanes/20% CCl$_4$ (v/v), followed by rinsing with hexanes and swabbing and rinsing with ethanol. This treatment was repeated, if necessary, to produce films of the expected thickness and with the expected contact angles.[9] The ellipsometric thickness of the layers thus formed was 2.5 nm, and the advancing contact angles of water and hexadecane were 112–114° and 42–43°, respectively. Receding contact angles for the two liquids on this surface were 101–106° and 40–42°, respectively. Silver substrates were prepared by the thermal evaporation of at least 90 nm of silver (99.99+%, Aldrich) onto a silicon wafer that had been treated with dilute aqueous hydrofluoric acid to remove the native oxide, and were broken into small pieces before use. To prepare SAMs, these pieces were treated for 1–3 h in ~13 mM solutions of hexadecanethiol (HDT, Aldrich) in ethanol, followed by rinsing with ethanol. The advancing contact angles of water and hexadecane on this surface were 112–115° and 44–46°, respectively, and the receding contact angles of these liquids were 100–103° and 37–40°, respectively. These contact angles are similar to those reported by others for ordered monolayers [see ref 18 and: Laibinis, P. E.; Whitesides, G. M.; Allara, D. L.; Tao, Y.-T.; Parikh, A. N.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 7152].
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(19) For comparison, more than 2.2 nm of growth is typically observed during the first adsorption cycle on Si/SiO$_2$.

(20) Iler studied the adsorption of charged colloidal particles onto oxide surfaces that had been rendered hydrophobic by the adsorption of surfactant monolayers.[13] These particles adsorbed by altering the structure of the physisorbed monolayers, or removing them altogether, in contrast to our findings for adsorption of PDDA and Laponite onto chemisorbed SAMs.

Figure 3. Schematic illustration of the adsorption of a composite film onto a SAM (a "macroscopic defect"). Polymer chains adsorbed at imperfections in the SAM during an initial treatment attract Laponite sheets during a subsequent treatment. As more cycles are performed, islands grow and then coalesce to form a film that covers the substrate, providing a surface upon which regular growth can occur.

coalesce to cover the low-energy surface of the SAM. By this mechanism of island growth and coalescence, depicted schematically in Figure 3, the entire surface can eventually be rendered active for adsorption. This creation of active sites starkly contrasts with the loss of sites that can occur during growth of multilayered films by alternate self-assembly and activation of molecular adsorbates. It is remarkable, in fact, that a film supported by such tenuous contacts to a surface can survive the extensive rinsing that follows each adsorption step. The similarity in eventual ellipsometric growth per cycle for films formed on SAMs and films formed on the bare substrates (i.e., the similarity in the slopes of the least-squares lines in Figure 2) suggests that after nucleation of the films on the SAMs, the growth mechanism is similar to that on the bare substrates. Ellipsometry measures an average thickness over a macroscopic area, however, and thus these results alone cannot conclusively rule out other modes of film growth, such as the formation of isolated particles of material on the sample surface.

To investigate these issues, we determined the topography of films formed on a SAM on Ag and on bare Ag (see Figure 4) using atomic force microscopy (AFM, Park Scientific Instruments SFM-BD2-210).[22,23] One would expect the process depicted in Figure 3 to produce tall, broad topological features that would not be present in a film formed on bare Ag. The larger features evident in Figure 4a are indeed consistent with the nucleation of the film at widely spaced imperfections in the SAM and eventual coverage of the surface by vertical and lateral growth of islands.[24] In light of the ellipsometric results, the absence of large, isolated particles in Figure 4a indicates that the material adsorbed as a film covering all, or nearly all, of the substrate. This observation effectively rules out any modes of growth that are radically different from that which occurs on the more favorable substrates.

We infer that the small differences in initial multilayer growth on the SAMs on Si/SiO$_2$ and on Ag (Figure 2) are due to a difference in the concentration of favorable adsorption sites on the two types of surfaces.[25] The greater the concentration of these sites, the more readily a film should adsorb. To test this hypothesis, we prepared an incomplete SAM on Si/SiO$_2$,[26] which should have a concentration of favorable sites intermediate between that of a complete SAM on this substrate and that of bare Si/SiO$_2$. The ellipsometric growth of a PDDA/Laponite multilayered film on this surface is

(21) To avoid ambiguity, we use the word "imperfections", rather than "defects", to refer to the flaws within the SAMs themselves that allow the nucleation of the multilayered films.

(22) Samples consisted of 10 adsorption cycles on a SAM on Ag and 8 adsorption cycles on a bare Ag surface. Both of these multilayered films had overall ellipsometric thicknesses of 21 nm. The slight apparent difference between the growth per cycle shown for the SAM on Ag in Figure 2 and that observed in this case can be attributed to differences in the ambient humidity on the days these samples were prepared (Kleinfeld, E. R.; Ferguson, G. S. *Chem. Mater.* **1995**, *7*, 2327). Images were obtained under ambient conditions in noncontact (attractive) mode using a Microlever (Si$_3$N$_4$) probe tip. The scan rate was 0.5 Hz, and the images were tilt-corrected. Repeated scans over the same area gave similar images, indicating that no damage to the samples was occurring.
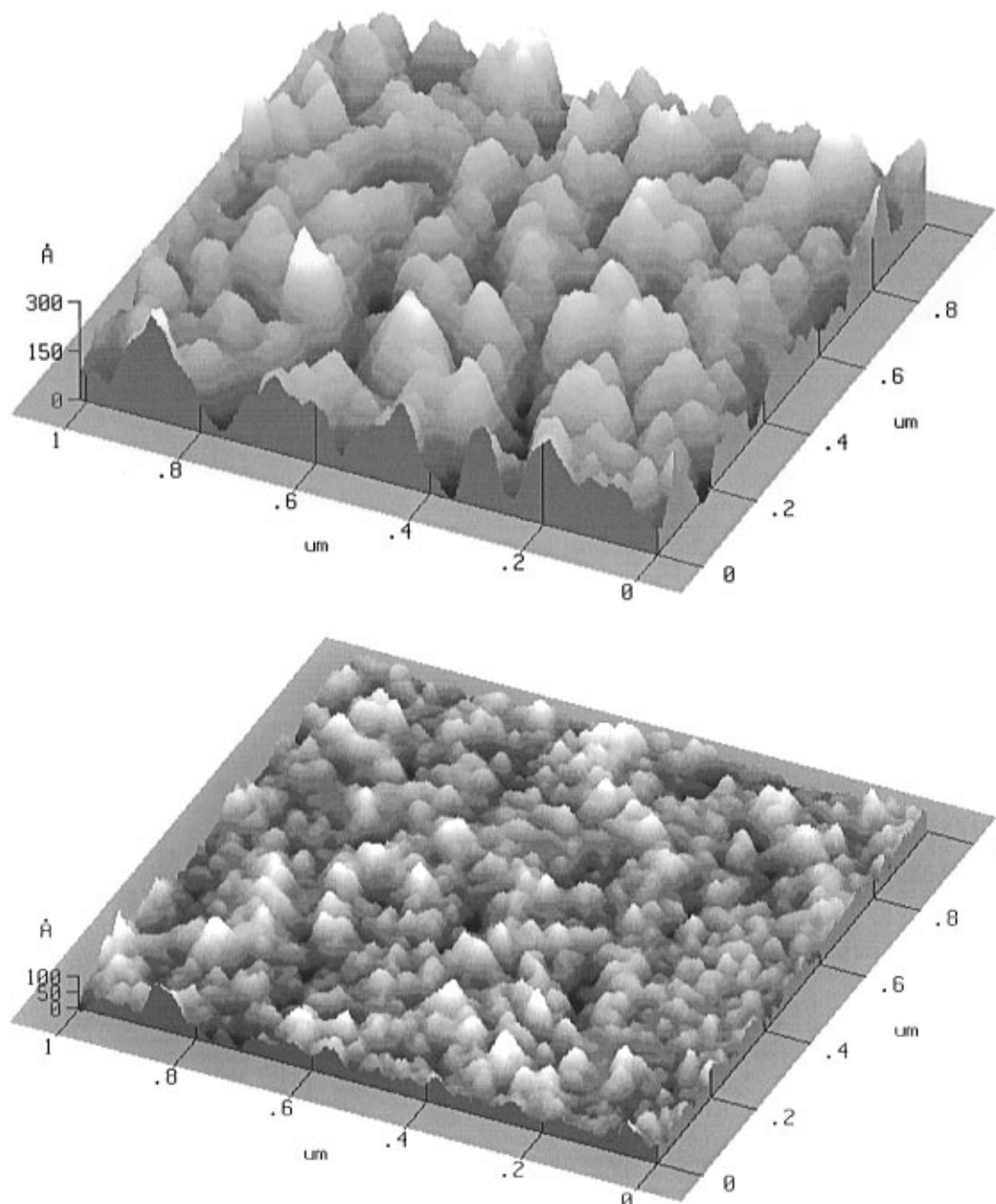
(23) The height scales in these AFM images provide information about the *relative* heights of features in the two samples; a value of 0 on those scales does not necessarily imply that the probe tip touched the Ag or SAM surface.

(24) Quantitative analysis of the data showed that the film formed on the SAM was more than twice as rough as the film formed on bare Ag (60 Å root-mean-square (rms) roughness vs 26 Å). An AFM image of a SAM-coated Ag surface, which should have a topology nearly identical with that of a bare Ag surface, was very similar in appearance to the image in Figure 4b and had an rms roughness of 18 Å. The uncertainty in these values of rms roughness is ±5 Å.

(25) In addition, image-charge interactions between the precursors and the substrates may be important, so that adsorption onto a certain imperfection in a SAM on Ag would be energetically more favorable than adsorption onto a similar imperfection in a SAM on Si/SiO$_2$.[18] The silicon used in this work (Wacker Siltronic) was p-doped and therefore conducting (resistivity 0.2–70 Ω cm) but was covered with an oxide approximately 1.5 nm in thickness. The force of attraction between a point charge and an infinite, planar, grounded conductor falls off as the inverse square of the distance between them (see: Griffiths, D. J. *Introduction to Electrodynamics*, 2nd ed.; Prentice Hall: Englewood Cliffs, NJ, 1989; pp 121–124).

Figure 4. AFM images, obtained in attractive mode, of (a, top) a 10-cycle film adsorbed onto a SAM on Ag; (b, bottom) an 8-cycle film adsorbed onto bare Ag.[22] The roughness of these surfaces is exaggerated by the difference between the vertical and lateral scales of length.

shown in Figure 2. As expected, regular growth began earlier on this surface (in the third cycle) than on the higher quality SAM on Si/SiO$_2$. The average thickness added per cycle eventually reached 2.9 nm, which is very similar to the growth observed on the other samples.

In summary, PDDA and Laponite adsorb at isolated imperfections in model inert surfaces, forming islands that later grow vertically and laterally until they coalesce. These results conclusively demonstrate that PDDA/Laponite films are able to heal any microscopic defects that occur in their formation. The fact that they

can form on model inert surfaces indicates that they should be expected to form on a great variety of other surfaces without the need for pretreatment. The ability to adsorb films on surfaces of low free energy also highlights the difficulties inherent in the creation of protective coatings, for example, in applications involving the prevention of protein adsorption or biofouling: even small imperfections in such coatings may result in their ultimate failure if the adsorption can be mediated by these sites.

(26) We produced incomplete SAMs on Si/SiO$_2$ by immersing cleaned silicon wafers in $\sim$7 mM OTS solutions in CHCl$_3$ for 5−7 min, producing films with an ellipsometric thickness of 1.3 nm. Advancing and receding contact angles of water on this surface, 105−108° and 99−101°, respectively, were lower than would be expected for complete SAMs. The advancing and receding contact angles of hexadecane were surprisingly high: 42−43° and 41−42°.