Layer-by-Layer Growth and Condensation Reactions of Niobate and Titanoniobate Thin Films

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Thin films were grown on amine-primed Si and glass substrates by sequential adsorption reactions of polyallylamine hydrochloride (PAH) and anionic colloids derived from $HTiNbO_5$ and $HCa_2Nb_3O_{10}$. The acid−base chemistry of polycation/polyanion adsorption was studied in detail for PAH/$HTiNbO_5$. The pK_a of PAH, defined as the pH at which it is half protonated, is 8.7. Titanoniobate colloids, prepared by reaction of $HTiNbO_5$ with tetra(*n*-butylammonium) hydroxide, TBA^+OH^-, are unilamellar at pH ≥ 8.5 and restack below pH 7.0. Efficient tiling of a PAH-terminated surface by a layer of unilamellar titanoniobate sheets occurs only at intermediate pH values (8.5−9.0). At lower pH, the colloid restacks on the surface, and at higher pH, only partial coverage by single sheets is observed by atomic force microscopy (AFM). At pH 8.5, high-quality multilayer films can be grown by sequentially adsorbing PAH with either the titanoniobate or niobate colloid. TGA/DTA studies of bulk PAH/titanoniobate intercalation compounds show that they decompose oxidatively to form $HTiNbO_5$ at 310−350 °C and that this decomposition is followed by interlayer condensation to make $Ti_2Nb_2O_9$. A similar process occurs in the PAH/titanioniobate multilayer films at 350 °C.

Introduction

An important theme of current microelectronics research is the development of techniques for making smaller circuit components. This miniaturization presents serious challenges in both the design of new kinds of logic devices and in the search for new materials and processing techniques. Thin-film capacitors made from high dielectric constant materials are currently under intensive investigation, because they are needed for solid-state dynamic random access memory (DRAM) devices. To make DRAMs with densities of 4 Gbit/chip, individual capacitors will need to be made as small as 0.10 μm^2 and will have capacitances of ∼14 fF.[1] For devices of this geometrical area the currently used silicon oxide/nitride composite layer cannot attain the required capacitance without unacceptably high leakage currents, because of its low dielectric constant ($\epsilon = 6$). As a result, since the mid-1980s there has been an increasing effort to investigate new materials, which have higher dielectric constants. Many ferroelectric ceramic perovskites, such as $BaTiO_3$, $SrTiO_3$, and $Pb(Ti_{1-x}Zr_x)O_3$, have very high dielectric constants (>1000) and are currently being studied for this purpose.[2] Recently, amorphous high dielectric films composed of Ti−Zr−Sn oxides have been identified by combinatorial screening.[3] Other oxide ceramics, particularly those derived from Ti, Ta, Nb, and Zn oxides, are also under investigation as promising high dielectric materials.[4]

The development of techniques for growing high dielectric thin films with complex stoichiometries at relatively low temperatures still remains a major research problem. Film growth techniques that are currently used include magnetron sputtering,[5] laser ablation,[6] CVD,[7] and sol−gel processing.[8] These techniques, however, usually require high processing temperatures, vaporization of the bulk dielectric material, or use of soluble precursors, which potentially exacerbate problems associated with unwanted elements in device fabrication. In the ideal case, thin-film dielectrics should be grown by low-temperature methods that lead reliably to very thin films of uniform thickness and composition over large areas. The precursors used should preferably expose the sample to no soluble or vapor-phase metal

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ions, such as alkali ions, which could be deleterious to the lifetime or performance of the device.

We recently developed a new low-temperature technique for growing unilamellar inorganic sheets on Si (or Au) surfaces using a self-assembly method.[9] Layered perovskite-type oxides can be prepared by high-temperature synthesis followed by aqueous proton exchange. The proton-exchanged compounds can then be exfoliated by an acid−base reaction, and unilamellar colloids of inorganic poly(anions) are thus obtained. By sequential adsorption of these two-dimensional colloidal polyanions and polymeric cations, thin films can be grown one layer at a time on a suitably primed substrate. This technique offers good control of film thickness over large areas. It is generally applicable to any lamellar transition metal oxide, including layered perovskites, some of which have interesting dielectric properties.[10] In this paper we examine the exfoliation of lamellar niobates and titanates and their layer-by-layer restacking on surfaces. We show that parameters such as pH are important determinants of the quality of oxide sheet monolayers and multilayer films. We further show that soft chemical reactions, which convert some of these lamellar materials into three-dimensional solids in bulk form, are also operative in intercalation compounds prepared as thin films.

Experimental Section

Instrumentation and Measurements. Transmission electron microscope (TEM) images were obtained with a JEOL 1200EXII microscope using 120 kV acceleration voltage and 80 μA filament current. Ellipsometric data were obtained with a Gaertner model L2W26D ellipsometer with HeNe laser (6328 Å) light. Typically, the film thicknesses at 5−7 spots on each sample were measured and averaged. Film thicknesses were calculated using a real refractive index of 1.54 and an imaginary refractive index of zero, which are typical values for organic films. Atomic force microscopy (AFM) was performed with a Nanoscope IIIA system. The AFM tips and cantilevers were made from microfabricated silicon nitride. All AFM images were collected in tapping mode. Tips were changed frequently to ensure reproducible resolution in the AFM images. Thin-film X-ray diffraction measurements were made with a Phillips X'Pert MPD diffractometer, using monochromatic Cu Kα radiation. Thermal gravimetric and differential thermal analyses (TGA/DTA) were performed on a DSC 220CU (Seiko Instruments) instrument. Elemental analyses for C, H, N, and Cl were performed by Atlantic Microlabs Inc., Norcross, GA.

Exfoliation of Layered Perovskites and Alkali Titanoniobates. The protonated lamellar compounds $HCa_2Nb_3O_{10}$ and $HTiNbO_5$ were prepared from the corresponding potassium compounds by ion exchange in aqueous 4 M HNO_3 or HCl at room temperature as described elsewhere.[10−12] The solids were separated from the supernatant solution, and the acid solution was renewed each day in order to ensure full exchange of alkali ions. The exchange was complete within 2 days. $HCa_2Nb_3O_{10}$ and $HTiNbO_5$ were exfoliated by adding a 5-fold molar excess of TBA^+OH^- (40 wt % in water, Aldrich), and the aqueous solutions were agitated at room temperature. Complete exfoliation of the solid, as evidenced by the disappearance of particles that precipitated rapidly, occurred within 24 h. The suspensions were stored at a relatively high concentration (4.5 mequiv/L) and high pH (~10.5) to avoid restacking of colloids. The resulting colloidal suspensions are turbid but quite stable, in that no precipitate forms in the quiescent liquid within 2 h. Precipitation occurs over periods of days, or upon centrifugation, but the suspension is easily restored by shaking. Before use, the colloids were typically diluted to 1 mequiv/L and the pH adjusted appropriately using 0.1 M HCl.

Exchange of Cs^+ by Na^+ in $CsPb_2Nb_3O_{10}$ was accomplished by stirring the $CsPb_2Nb_3O_{10}$ powder in a saturated NaCl solution for 3 days at room temperature. The solid was separated from the supernatant solution, and the NaCl solution was renewed each day. $NaPb_2Nb_3O_{10}$ was exfoliated by adding a 10-fold molar excess of *n*-propylamine and agitating the aqueous solution at room temperature for 2 days.

Thin-Film Preparation. Polished (100) Si wafers (p-type, $(3.5-9.5) \times 10^{15}$ carriers/cm^3, 1.5−4 ohm/cm resistivity) were obtained from Research and PVD Materials Company. The wafers were cut into 0.5×1.0 cm^2 rectangles and sonicated in CCl_4 for 15 min, and then were rinsed with 2-propanol and water. They were then sonicated in a hot piranha solution (3:1 v:v concentrated H_2SO_4 and 30% H_2O_2—CAUTION—reacts violently with organic compounds) for 30 min and rinsed with copious amounts of water. The cleaned wafers were rinsed successively with methanol, 1:1 methanol/toluene, and toluene, and then immersed in a 2 wt % (4-aminobutyl)dimethylmethoxysilane (United Chemical Technologies, Inc.) solution in toluene under Ar. This surface priming reaction was allowed to proceed inside a desiccator overnight. The Si wafers were then washed twice in toluene, once in 2-propanol, and once in methanol, and were dried under Ar.

Borosilicate glass microscope cover slips were cleaned and primed with (4-aminobutyl)dimethylmethoxysilane in the same way, except that the final rinse sequence was performed with absolute ethanol, then with 2-propanol, and finally with water. The glass samples were then immersed immediately in a 25 mequiv/L poly(styrenesulfonate) sodium salt (PSS, Acros Chemicals, MW = 70 000) solution for 20 min, and rinsed with water. They were then immersed in a 25 mequiv/L solution of poly(allylamine hydrochloride) (PAH, Aldrich, MW = 50 000−65 000) for 20 min and rinsed with water. These adsorption steps were repeated to produce a PSS/PAH/PSS/PAH multilayer film on top of the amine priming layer. The purpose of this polyanion/polycation film is to cover any defects or incompletely primed areas of the substrate. Both polyelectrolyte solutions were made by dissolving the solid polymer at 50 °C. The solutions were allowed to stand for 10 h and were passed through a 0.2 μm filter before use.

Multilayer colloid/polycation films were typically grown on Si in 15 min adsorption cycles, using 0.01 mequiv/L aqueous PAH to form the polycation layers. The substrates were washed with flowing water between adsorption steps. For the glass/amine/PSS/PAH/PSS/PAH substrates the duration of the colloid monolayer adsorption step was 30 s. The samples were then rinsed with a 1 μM solution of $TBA^+HCO_3^-$ adjusted to the same pH as the colloid using dilute HCl or TBA^+OH^-, and rinsed with water.

Preparation of Bulk $HTiNbO_5$/PAH Intercalation Compounds. Bulk analogues of the sequentially adsorbed $HTiNbO_5$/PAH thin films were prepared using stoichiometric and excess quantities of PAH. In the former case, a titanoniobate colloid (4.5 mequiv/L, pH 8.5, 50 mL) and an unbuffered PAH solution (0.010 M, 23 mL) were mixed rapidly. In the latter, 120 mL of 0.045 M PAH solution (5.4 mequiv) was adjusted to pH 8.5 using TBA^+OH^-. Thirty milliliters of the exfoliated titanoniobate colloid (pH 9.0, 40 mequiv/L, 1.2 mequiv) was added dropwise to the PAH solution with vigorous stirring over the course of 5 min. In both instances, a gelatinous white solid precipitated immediately, and the resulting suspension was stirred overnight at 40 °C. The gellike precipitate was collected

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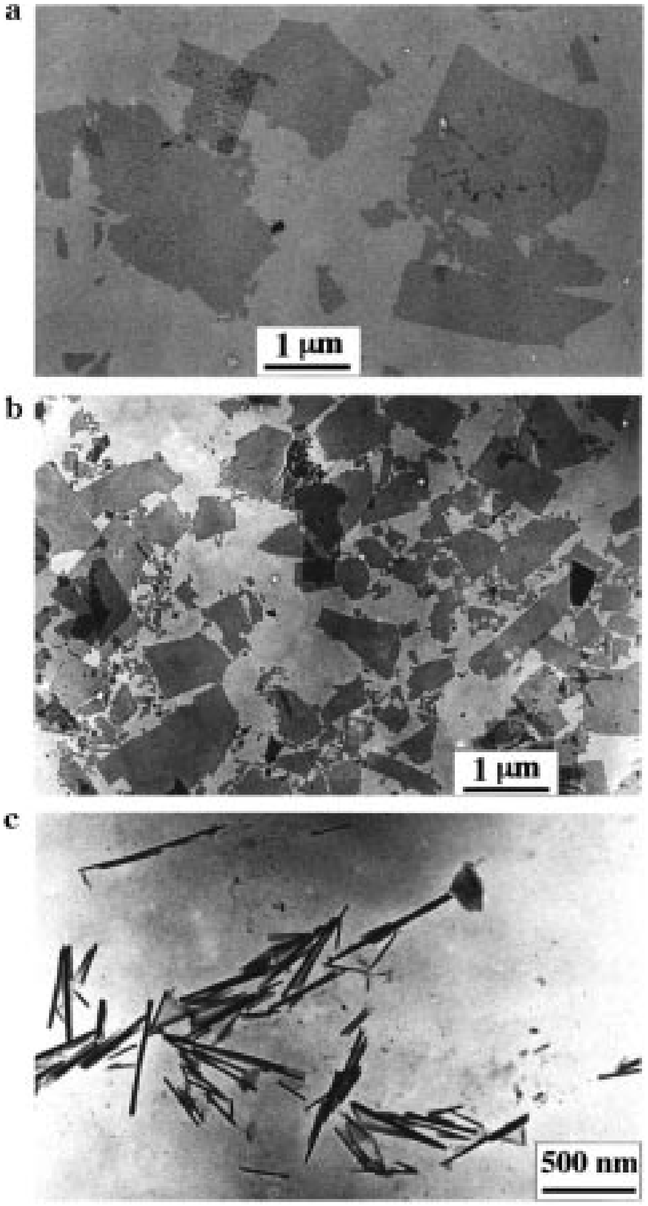

Figure 1. TEM images of exfoliated (a) $TiNbO_5^-$, (b) $Ca_2Nb_3O_{10}^-$, and (c) $Pb_2Nb_3O_{10}^-$ sheets on the surface of a Formvar-coated Cu grid. In panel c, $CsPb_2Nb_3O_{10}$ was first ion-exchanged to make $NaPb_2Nb_3O_{10}$. $NaPb_2Nb_3O_{10}$ was then exfoliated by addition of aqueous *n*-propylamine.

by centrifugation and rinsed three times with water, and then dried in air at ambient temperature.

Results and Discussion

Exfoliation of $HTiNbO_5$ and the Dion−Jacobson Phases, $HM_2Nb_3O_{10}$ (M = Ca, Pb). Rebbah and coworkers previously reported the exfoliation of $HTiNbO_5$ using aqueous ethylamine.[13] With the strong base intercalant TBA^+OH^-, delamination of $HTiNbO_5$ occurs when more than about 45% of the acidic protons are neutralized. Figure 1 shows a TEM image of exfoliated titanoniobate sheets prepared by stirring solid $HTiNbO_5$ with excess aqueous TBA^+OH^- at 22 °C. The observation of many $TiNbO_5^-$ sheets with similar contrast suggests that the colloid is unilamellar, and this is supported by AFM experiments (see below), which showed that the suface-bound sheets were ~1 nm thick. The lateral dimensions of the sheets range from about 100 nm to 2 μm. Many of the sheets have irregular shapes and curved edges, but some have sharp edges, suggesting preferential cleavage along certain crystal planes. Figure 1 also shows a TEM image of similarly exfoliated sheets of the three-layer Dion−Jacobson phase $HCa_2Nb_3O_{10}$. The colloidal particles are similar to those obtained by Treacy et al., who used amine surfactants to exfoliate $HCa_2Nb_3O_{10}$ and related materials.[14] The sheets again show distinct edges that suggest cleavage along preferred directions. Similar results were obtained with the four-layer Dion−Jacobson phase $KCa_2NaNb_4O_{13}$, which was first acid-exchanged in 4 M HCl for 4 days to yield $HCa_2NaNb_4O_{13}$, and then exfoliated with excess TBA^+OH^-.

In contrast to isostructural $HCa_2Nb_3O_{10}$, which intercalates and exfoliates within minutes at room temperature, $HPb_2Nb_3O_{10}$ is unreactive with TBA^+OH^-, even when heated to 60 °C for several days. Apparently the interlayer hydrogen bonding in the Pb compound is sufficiently strong to prevent reaction even with strong base. An alternative intercalation/exfoliation strategy was therefore attempted in order to avoid the unreactive proton-exchanged phase. $CsPb_2Nb_3O_{10}$ was first exchanged with Na^+, which is more readily hydrated than Cs^+. The Na^+-exchanged compound was then exfoliated using an aqueous solution of *n*-propylamine. Figure 1c shows a TEM image of the exfoliated $Pb_2Nb_3O_{10}^-$ sheets in aqueous solution. Interestingly, the sheets are coiled up to form high aspect ratio rolls which are microns in length and 20−40 nm in diameter. Similar phenomena have been observed for single sheets derived from $K_4Nb_6O_{17}$[15] and for fibrous silicates such as halloysite.[16] In both of these cases the sheets are asymmetric in the parent crystal, and their curvature in the colloid relieves built-in strain. In the case of $Pb_2Nb_3O_{10}^-$, however, the sheets are centrosymmetric in bulk $CsPb_2Nb_3O_{10}$. The breaking of this symmetry is apparently energetically favorable for single sheets of $Pb_2Nb_3O_{10}^-$. $HPb_2Nb_3O_{10}$ is a high dielectric material ($\epsilon \approx 150$ at room temperature),[10] and it is possible that the symmetry breaking relieves strain by distorting the NbO_6 octahedra cooperatively, as happens in displacive ferroic phase transitions in three-dimensional perovskites.[17]

Acid−Base Titrations of $HTiNbO_5$ and Poly(allylamine hydrochloride), PAH. The layer-by-layer assembly of polyelectrolyte thin films requires that the two components (e.g., inorganic sheets and polycations) bear opposite charge under the conditions (pH, concentration, temperature) of film growth.[18] To choose these conditions properly, it is important to understand the acid−base properties of the components, particularly when one or both are weak polyacids/bases.

Figure 2 shows acid−base titration curves for PAH and exfoliated $HTiNbO_5$. In the case of PAH, a clear

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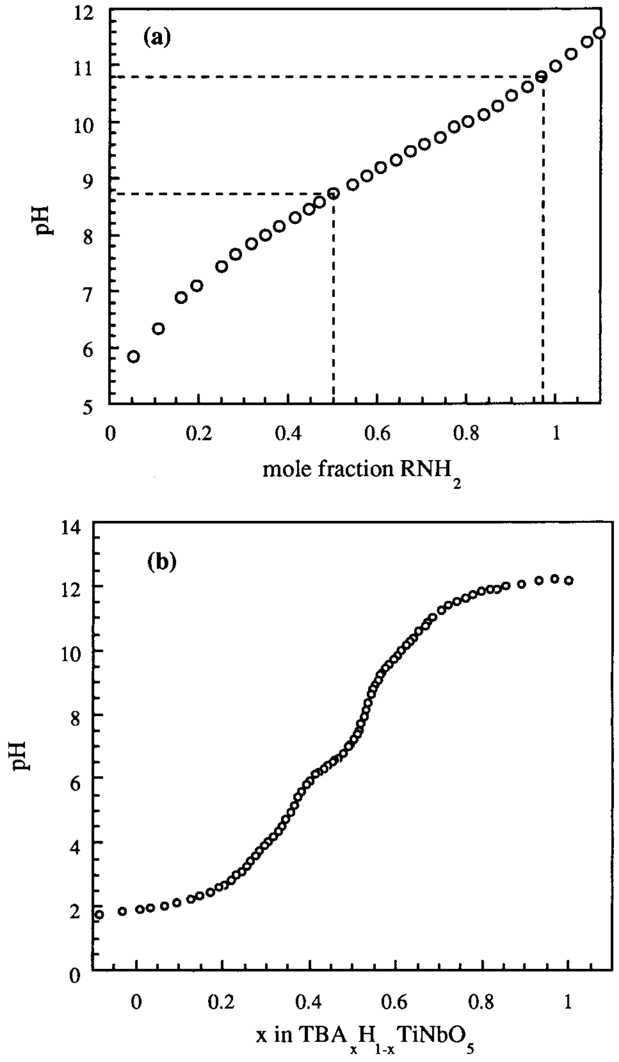

Figure 2. Acid−base titration curves of polyelectrolytes: (a) poly(allylamine hydrochloride), PAH, titrated with aqueous TBA^+OH^- [dotted lines indicate pK_a values for monomeric aliphatic amines (10.8) and for the polymer (8.7)]; (b) HCl titration of $HTiNbO_5$ exfoliated by reaction with excess TBA^+OH^-.

polyelectrolyte effect is observed. That is, the buffer region of the titration curve is spread out over several pH units. Also, the apparent pK_a of the polymer, defined as the point at which half of the amine groups are protonated, is 8.7. This is 2.1 pH units lower than the typical pK_a of an aliphatic amine, which is ∼10.8. The lower pK_a reflects the fact that cation−cation repulsion in the polymer makes it progressively more difficult to protonate as the mole fraction of protonated amine groups increases. At pH 10.8, only about 2% of the amine groups in the polymer are protonated. At the monomer pK_a, therefore, one would not expect strong interactions between PAH and polyanion sheets.

For the titanoniobate colloid, titration with acid causes restacking to yield first the TBA^+ intercalation compound, and eventually the proton-exchanged restacked solid $HTiNbO_5$. This titration curve, plotted as TBA^+ mole fraction in $TBA_xH_{1-x}TiNbO_5$, is similar to that observed with α-zirconium phosphate colloids.[19]

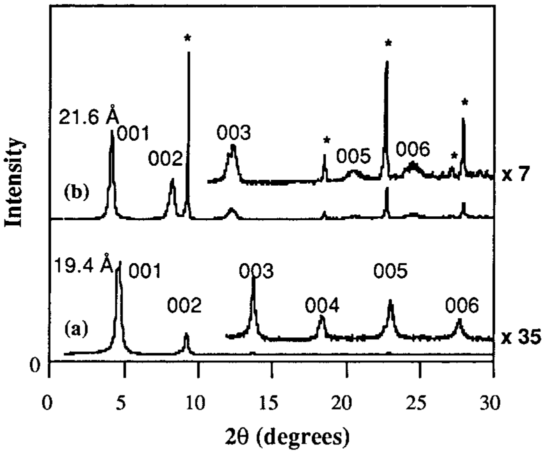

Figure 3. X-ray diffraction powder patterns of dried $TBA_xH_{1-x}TiNbO_5$ colloids on Si; (a) pH 8.5 colloid and (b) the same colloid with 20 equiv of TBA^+Br^- added per mol $TiNbO_5^-$. In panel b, peaks marked with an asterisk (*) are from solid TBA^+Br^-.

Briefly, there are two equivalence points in the basic region of the curve. The most pronounced of these, centered at pH 8.5 and $x = 0.54$, corresponds to a single-phase unilamellar colloid. A second colloidal phase, apparently with a denser packing of TBA^+ ions on the two sides of the sheets, is indicated by a flat region of the titration curve centered at pH 10.0, $x = 0.61$. Figure 3 shows powder X-ray diffraction patterns of the pH 8.5 colloid, dried at 60 °C on a silicon wafer, and the same colloid with 20 equiv of TBA^+Br^- added per mol $TiNbO_5^-$. These colloidal films of $TBA_xH_{1-x}TiNbO_5$ are well-ordered in the stacking direction, as evidenced by high order 00*l* reflections in the patterns, but there is apparently no ordering in the lateral dimensions. The layer spacings (19.4, 21.6 Å) represent the 8 Å $TiNbO_5^-$ layer and a loosely or tightly packed bilayer of TBA^+ cations, respectively.[20]

Below pH 7 in the titanoniobate titration curve, the pH equilibrates slowly (≥10 min) after each addition of acid, and there is a flat region of the curve, indicating the coexistence of a colloidal phase and the solid TBA^+ intercalation compound. The appearance of a precipitate in this pH region is consistent with this interpretation of the titration curve. Finally, there is a gradual decrease in pH with no apparent inflection points as the composition of the intercalation compound changes between $x = 0.4$ and $x = 0$. An important conclusion from this titration with regard to layer-by-layer assembly of thin films is that the unilamellar colloid only exists as a pure phase at pH ≥ 8.5.

AFM of $(TBA^+)_xH_{1-x}TiNbO_5$ Monolayers. AFM images of $(TBA^+)_xH_{1-x}TiNbO_5$ monolayers on glass/amine/$(PSS/PAH)_2$ substrates underscore the importance of acid−base equilibria on the colloid self-assembly process. Figure 4 shows images in three representative pH regimes. At high pH (upper image, pH 10.4), the colloid is well-dispersed into single sheets, but the PAH monolayer on the surface is largely deprotonated. Consequently, there is only a weak interaction between the surface and the polyanion sheets, and sparse coverage is observed. At low pH (lower image, pH 6.3) there

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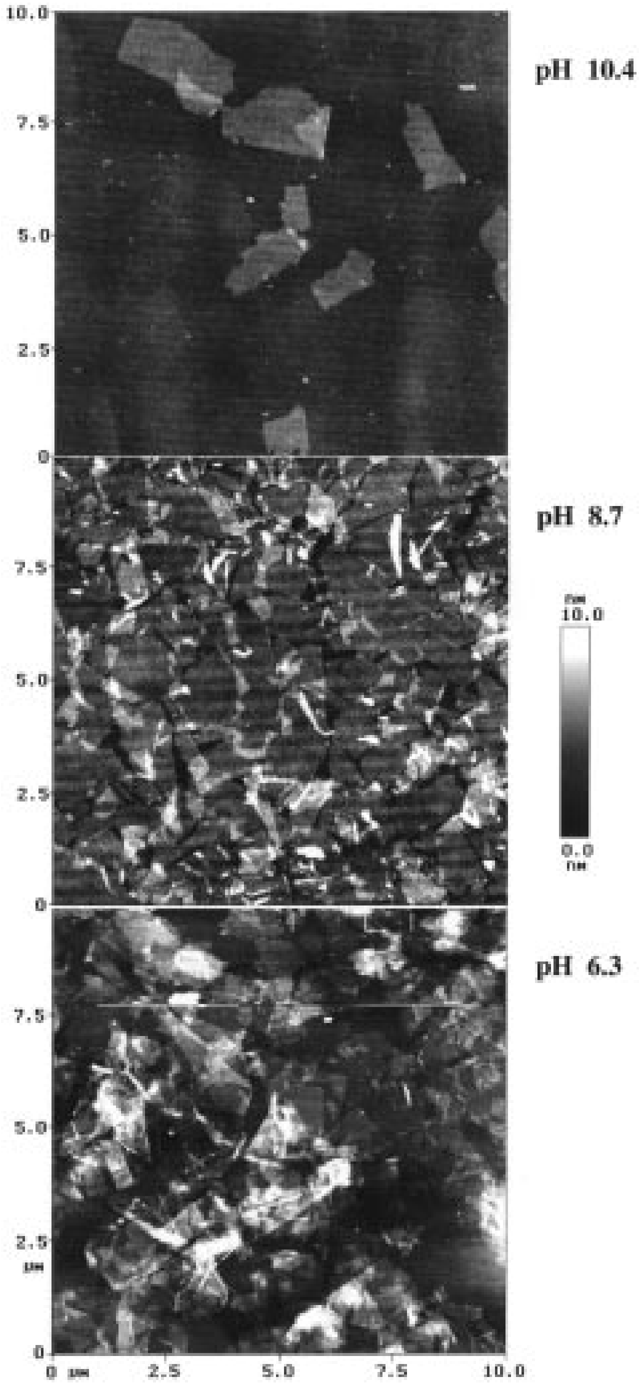

Figure 4. AFM images of the first layer of $TiNbO_5^-$ sheets adsorbed on glass/amine/$(PSS/PAH)_2$ substrates at different pH values: top, pH 10.4; middle, pH 8.7; bottom, pH 6.3.

is sufficient positive charge on the surface to bind the colloid everywhere, but the sheets tend to restack into a multilayer film. This behavior is consistent with the titration curve of $HTiNbO_5$, which shows restacking below pH 7.

Good monolayer films can be obtained only at intermediate pH. At pH 8.7 (middle image, Figure 4), the PAH layer is ~50% protonated and, therefore, has sufficient charge density to displace TBA^+ ions from the colloid. At this pH, the colloid is also substantially unilamellar. The AFM image shows that the surface is densely tiled by sheets, although some gaps (black areas) and bilayer patches (white areas) are apparent. The dense tiling and minimal overlap of neighboring sheets imply that the sheets must have some lateral mobility, or they must adsorb and desorb rapidly during the 30-s adsorption step. Some of the larger sheets (>2 µm in size) in the image are torn, but the pieces are still in contact on the surface. The probable cause of this effect is lateral stress during the drying process. It is unlikely that the stress is caused by adsorption, because dense tiling implies lateral mobility or reversible adsorption. In neither case would one expect pieces of a torn sheet to remain associated with each other on the surface.

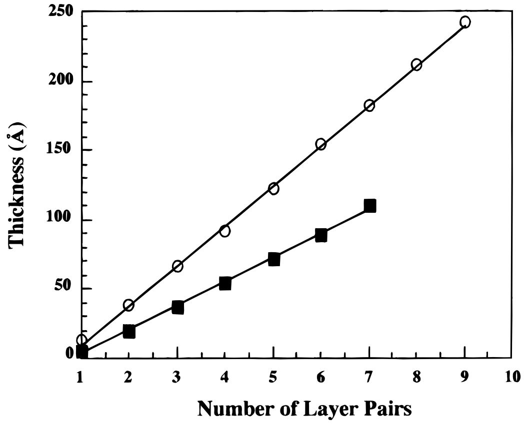

Figure 5. Ellipsometric data for $HCa_2Nb_3O_{10}$ (○) and $HTiNbO_5$ (■) multilayer films on amine-derivatized Si/SiO_x. Lines represent best fits to the data using $n = 1.54$, and give layer pair thicknesses of 27.4 and 16.3 Å.

Ellipsometry and XRD of $TiNbO_5$/PAH and Dion–Jacobson Multilayer Thin Films. Both the $TiNbO_5^-$ and $Ca_2Nb_3O_{10}^-$ colloids form dense monolayers on PAH-terminated surfaces at pH 8.5–9.0. Only a single layer of sheets is adsorbed, because under these conditions the colloid is unilamellar and therefore the net interaction between sheets is repulsive. However, this monolayer readily exchanges its TBA^+ counterion layer for polycations such as PAH. The polyanion/polycation process can be repeated to build up the desired number of layers as in similar polyelectrolyte deposition strategies.[9,16,21] Figure 5 shows that the ellipsometric thickness increases linearly, 16.3(3) Å per layer pair for $TiNbO_5$/PAH and 27.4(3) Å for $Ca_2Nb_3O_{10}$/PAH. The thicknesses of the individual colloid sheets are approximately 8 and 13 Å,[22] and allowing 5 Å for a single, uncoiled PAH layer,[23] the bilayer pair thicknesses derived from ellipsometry are slighly larger than those expected for single sheets.

Figure 6 shows X-ray diffraction patterns obtained from 4- and 10-bilayer $TiNbO_5$/PAH films on Si. The films are well-ordered in the stacking direction, as evidenced by the appearance of a relatively strong Bragg peak, and in the thicker film by a second-order peak as well. These Bragg peaks (14.4–14.5 Å) provide a check of the ellipsometric data and indicate that the derived value of 16.3 Å per layer pair may reflect an underestimation of the film refractive index.

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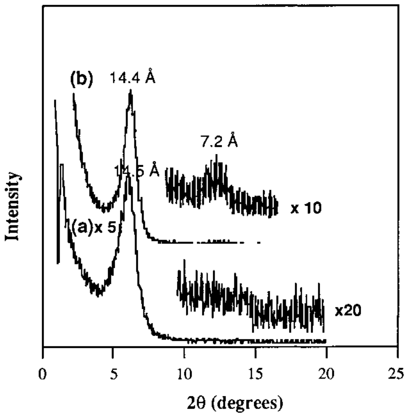

Figure 6. X-ray diffraction patterns of (a) 4- and (b) 10-bilayer $TiNbO_5$/PAH films on Si.

Bulk $TiNbO_5$/PAH intercalation compounds were made for comparison purposes by combining the exfoliated titanoniobate colloid with aqueous PAH. In one experiment, stoichiometric amounts of the colloid and PAH were combined. The flocculent precipitate, which formed immediately, was filtered and dried and gave a 15.7 Å diffraction line. The fact that higher order 00*l* lines are not observed in this pattern indicates that the rapidly restacked compound is very poorly ordered. Elemental analysis of this $TiNbO_5$/PAH intercalation compound (found, after drying at 150°: C, 17.67; H, 3.61; N, 2.02; Cl, 0.00%) indicated an approximate composition $H_{0.58}(PAH)_{0.19}(TBA)_{0.23}TiNbO_5$ (calculated: C, 17.83; H, 3.60; N, 2.05%). This restacking reaction, starting from PAH in its fully protonated form, results in the displacement of only about half of the TBA^+ ions from the colloid and leaves a material in which about half of the ion exchange sites are protonated. In a second experiment, the colloid was added dropwise to a solution containing excess PAH, which had been adjusted to pH 8.5 with TBA^+OH^-. In this case elemental analysis (found, after drying at 225°: C, 18.46; H, 4.22; N, 5.64; Cl, 2.96%) is consistent with a formulation $(PAH)_{1.22}(TBA)_{0.08}(TiNbO_5)(Cl)_{0.27}$ (calculated: C, 18.62; H, 3.97; N, 5.71; Cl, 3.00%). With excess PAH, the TBA^+ ions and protons are displaced more efficiently, but some PAH^+Cl^- is entrained in the solid. The higher PAH content of this intercalation compound can also be attributed to the fact that the polymer is not fully protonated at pH 8.5, and so more of it is needed to charge compensate the sheets. The increased layer spacing (22 Å) of this intercalation compound is also consistent with the presence of a relatively thicker layer of PAH between each pair of $TiNbO_5$ sheets.

We note that in neither of these cases does the preparation of the bulk intercalation compounds truly mimic that of the thin films. In the case of the thin films, the substrate is sequentially reacted with a vast excess of either reagent (titanoniobate colloid or PAH) under conditions of controlled pH, and excess reagents are washed off before the next layer is added. The displacement of counterions such as Cl^- and the full exchange of TBA^+ ions are uncomplicated by kinetic effects. On the other hand, the bulk solids restack rapidly before ion exchange equilibrium is reached. The fact that the bulk solids show only one Bragg diffraction peak, whereas the 10-layer thin film shows two (Figure 6), is consistent with the lower degree of order of the former.

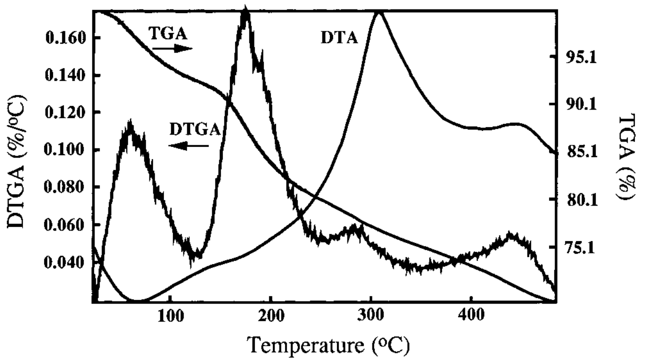

Figure 7. TGA/DTA diagram of PAH-intercalated $HTiNbO_5$ heated 20 °C/min in air. The dotted line is the first derivative of the TGA curve.

Table 1. Elemental Analysis of PAH-intercalated $HTiNbO_5$, ($H_{0.58}((PAH)_{0.19}((TBA)_{0.23}TiNbO_5$) Heated in Air to Temperatures Corresponding to Decomposition Steps Observed by TGA (Figure 7)

	C%	H%	N%
PAH	36.37	8.56	14.19
$HTiNbO_5$	0.00	0.45	0.00
PAH/$HTiNbO_5$ (150 °C, 2 h)	17.67	3.61	2.02
PAH/$HTiNbO_5$ (350 °C, 24 h)	0.67	0.30	0.13
PAH/$HTiNbO_5$ (450 °C, 6 h)	0.40	0.24	0.00

Condensation of PAH/$TiNbO_5$ Intercalation Compounds and Thin Films to $Ti_2Nb_2O_9$. "Chimie douce" condensation reactions convert some lamellar solids into three-dimensional frameworks. For example, both $HTiNbO_5$ and $HCa_2Nb_3O_{10}$ dehydrate topochemically to make, respectively, $Ti_2Nb_2O_9$[24] and $Ca_4Nb_6O_{19}$.[10] In the case of polycrystalline starting materials this transformation eliminates some sources of dielectric loss, such as inter- and intragrain proton mobility. An interesting question is whether a similar transformation can occur in restacked intercalation compounds and multilayer thin films.

Thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) experiments conducted in air with the bulk $TiNbO_5$/PAH intercalation compound $H_{0.58}(PAH)_{0.19}(TBA)_{0.23}TiNbO_5$ show four distinct decomposition steps (Figure 7). The first occurs at about 60 °C. DTA shows that this is an endothermic phase transition and is most likely caused by the desorption of water from the sample. The second transition is observed at about 180 °C, and DTA shows a small exothermic peak. The third transition happens at about 310 °C and is exothermic. After this transition (350 °C), elemental analysis (Table 1) shows that most of the PAH and TBA have decomposed, leaving protons and possibly some NH_4^+ ions as the charge compensating species between the layers. At this temperature, one also expects the condensation reaction of $HTiNbO_5$ to $Ti_2Nb_2O_9$ to occur. The last, weakly exothermic transition is observed at about 450 °C. Elemental analysis shows the loss of the small amount of remaining nitrogen in the compound during this transition.

The decomposition steps for the $(PAH)_{1.22}(TBA)_{0.08}(TiNbO_5)(Cl)_{0.27}$ intercalation compound are affected by the presence of excess PAH. TGA/DTA analysis shows that the oxidation of PAH does not begin until 410 °C

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(24) Rebbah, H.; Desgardin, G.; Raveau B. *Mater. Res. Bull.* **1979**, *24*, 1125.

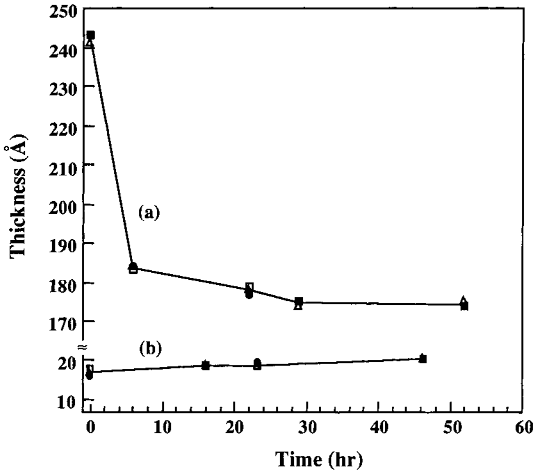

Figure 8. Ellipsometric thicknesses of (a) a 10-bilayer $TiNbO_5$/PAH film on Si vs heating time at 350 °C, and (b) a Si/SiO_2 substrate subjected to the same conditions. The markers represent different measurements and the line represents the average results. Thicknesses were calculated from ellipsometric measurements using a film refractive index $n_f = 1.54$.

and, according to CHN analysis, is complete before the resulting $HTiNbO_5$ dehydrates at 475 °C. Excess PAH appears to impede the collapse of layers until it is completely removed. Interestingly, the higher degree of protonation in the $H_{0.58}(PAH)_{0.19}(TBA)_{0.23}TiNbO_5$ intercalation compound allows the condensation reaction to occur at lower temperatures, possibly by nucleation of the collapsed $Ti_2Nb_2O_9$ phase from small domains of $HTiNbO_5$. This process may promote the oxidation of the TBA ions and PAH polymer.

Figure 8 shows the results of heating a 10-bilayer $TiNbO_5$/PAH film on Si to 350 °C, the temperature at which the conversion from $HTiNbO_5$ to $Ti_2Nb_2O_9$ occurs in the bulk $H_{0.58}(PAH)_{0.19}(TBA)_{0.23}TiNbO_5$ intercalation compound. There is a rapid initial decrease in film thickness, which ultimately stabilizes at about 70% of its original value. A control experiment (Figure 8b) shows that the thickness of the SiO_2 layer on the Si substrate is unaffected by the same heat treatment. Therefore, the thickness decrease reflects a contraction of the $TiNbO_5$/PAH film. The condensation of 10 $TiNbO_5$/PAH layers to $Ti_2Nb_2O_9$ should cause a thickness decrease of 10(16.3−15.1/2) = 88 Å, since the lattice spacing of $Ti_2Nb_2O_9$ is 15.1 Å.[25] This is slightly more than the thickness change (68 Å) observed in Figure 8. It appears therefore that a condensation reaction similar to that observed in the bulk intercalation compound occurs in the turbostratically disordered thin films, following decomposition of intercalated PAH.

Conclusions

One of the key findings of this study is that pH control is essential in the colloid self-assembly process, particularly when the charge-compensating polycation is also subject to acid−base equilibrium. One must find conditions under which the colloid is unilamellar (sufficiently high pH) and the polymer is positively charged (sufficiently low pH). If both of these conditions can be fulfilled simultaneously, then single, dense monolayers of each component can be sequentially adsorbed.

With both thin films and bulk intercalation compounds prepared from PAH and titanoniobate colloids, a series of thermal decomposition reactions occur, and the last step, which occurs at about 350−475 °C, corresponds to the conversion of $HTiNbO_5$ to $Ti_2Nb_2O_9$. With polycrystalline $HTiNbO_5$, this is known to be a topotactic condensation reaction. With turbostratically ordered intercalation compounds and thin films, the process cannot be entirely topotactic. Nevertheless, this finding suggests that it may be possible to carry out similar condensation reactions in thin films with other lamellar oxides and that this process may be a useful route to dielectric or ferroelectric thin films. These possibilities are currently under investigation.

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(25) Marchand, R.; Brohah, L.; Tournoux, M. *Mater. Res. Bull.* **1980**, *15*, 1129.