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Research Article

Synthesis of Nanostructured Nanoclay-Zirconia Multilayers: a Feasibility Study

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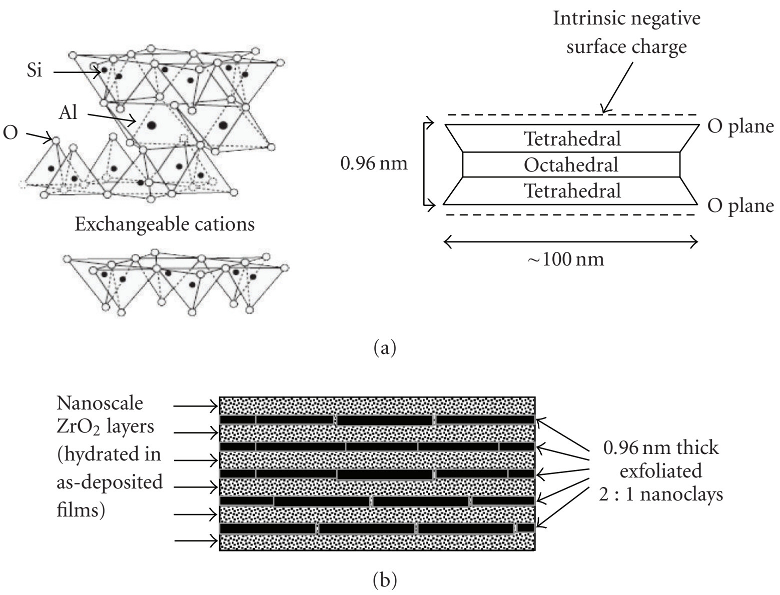
This paper reports the first effort to synthesize a new class of inorganic nanostructured materials consisting of alternating ultrathin layers of nanoclays and oxide ceramics. A novel solution-based layer-by-layer (LBL) deposition technique was developed to prepare multilayers of hydrated Zr cations and nanoclays. This LBL deposition technique is devised by integrating an electrostatic-mediated dip coating method for making nanoclay-polymer multilayers with a successive ionic layer adsorption and reaction method for making ultrathin oxide films. Nanostructured clay-zirconia multilayer composites formed through subsequent annealing. Characterization by scanning electron microscopy, energy dispersive X-ray spectroscopy, and X-ray diffraction confirmed that these films are uniform and crack-free, consist of no detectable impurities, and possess nanoscale-layered structure. The incorporation of nanoclays facilitates the electrostatic-mediated assembling of multilayers, enhances the structural integrity, and provides a generic framework to construct functionally graded materials. Potential applications are envisaged.

1. INTRODUCTION

The last decade has seen tremendous developments in the "wet" colloid chemical synthesis of nanosized and nanostructured materials, which was inspired by "biomineralization and hierarchically organized self-assembly" [1]. This wet synthesis technique utilizes alternating layer-by-layer (LBL) deposition process, which is enhanced by electrostatic assembling or surface-mediated adsorption and reaction. It has several major advantages, such as relative ease of preparation, low cost, and high versatility. Through this technique, a variety of nanostructured materials with improved properties or enhanced functionalities have been developed, including inorganic [2, 3] or hybrid organic-inorganic [4] films. In particular, inspired by the special mortar-brick nanostructure of nacre and its superior mechanical properties, hybrid multilayers consisting of alternating organic polymer and inorganic nanoclay layers have been made by an LBL deposition and assembly method [5, 6]. This method was modified from a more general method for making polyelectrolyte multilayers where substrates are alternately dipped into polycation and polyanion solutions to form polyelectrolyte thin films [7].

In parallel, a successive ionic layer adsorption and reaction (SILAR) method [8–10] was developed initially for the deposition of sulfide films. The SILAR method grows sulfide thin films by repeating deposition cycles consisting of four steps: dipping in cationic precursor solutions for adsorption of cations, rinsing to remove physisorbed cations, dipping into anionic (S^{2-}) solutions to form a monolayer or submonolayer of sulfides, and rinsing again. This SILAR technique has recently been adapted to deposit oxide (e.g., ZnO) films [9, 10]. Notably, this technique has been used for making ultrathin (e.g., 1–10 nm) gate dielectric oxide films [11, 12] and combined with a hydrothermal annealing process for low-temperature synthesis of nanocrystalline oxide films [13]. More recently, the feasibility of a modified SILAR technique without rinsing steps to prepare thin zirconia films has been reported [14] and the associated film growth kinetics has been studied [15]. The latter approach can be regarded as a surface hydrolysis and precipitation process assisted by electrostatic interactions [14, 15].



(a)

(b)

Figure 1: (a) The structure of 2 : 1 clay nanoplatelets exfoliated from MMT. (b) A targeted multilayer structure to be synthesized using a new LBL assembling technique via making use of the intrinsic negative surface charges and unique platy shape of nanoclays (as shown in (a)). In principle, the thickness and chemical composition of each nanometer-thick oxide layer can be tuned individually, offering versatility in engineering these nanostructured films with a wide range of potential applications to be explored in future studies.

A key underlying mechanism in the wet chemical construction of nanomaterials is the solution-based self-assembly aided by electrostatic attraction force between oppositely charged components (e.g., ions, polyions). The use of platy-shaped clay nanoplatelets with intrinsic, permanent negative surface charges in constructing nanostructured multilayers is an innovation to extend the capabilities of the conventional ion/polyion aided self-assembly techniques. Clay minerals are hydrous layered aluminosilicates, and montmorillonite (MMT) is a swelling clay mineral consisting of 2 : 1 layers (i.e., 2 tetrahedral and 1 octahedral sheets per layer, as shown in Figure 1(a)). These 2 : 1 layers can be separated in Na^+ or Li^+ rich solutions forming exfoliated clay nanoplatelets of ~1 nm in thickness. The permanent negative surface charges of nanoclays not only promote the electrostatic self-assembly process and its efficiency, but also render a high lateral bond strength within the constructed multilayers or their precursors [1]. In addition, the high aspect ratio of platy nanoclays provides an ideal planar surface for self-assembly and growth of other nanomaterials. To date, hybrid inorganic clay and organic polymer (including biopolymer) nanostructured multilayers have been developed [16], but development in making nanoclay-based inorganic nanocomposites or multilayers has not been reported. Due to the inherent thermal and chemical instability of organic polymers, hybrid organic and inorganic multilayers have limitations in some specialized applications, such as in high-temperature environments. In this study, we attempt to develop a new class of inorganic oxide-clay nanostructured multilayers.

The paper presents the preliminary findings of this research with a particular focus on the feasibility of making hydrated inorganic oxide-clay nanostructured multilayers using the newly developed solution-based LBL synthesis technique. The ultimate goal of this study is to develop purely inorganic, nanostructured nanoclay-oxide multilayers, as shown in Figure 1(b). Zirconia is chosen as the model oxide because we have recently developed a modified SILAR technique to make pure or doped zirconia films [14] and a relevant film growth model [15]. Zirconia thin films have a wide variety of applications, such as protective coatings, insulating or dielectric ceramic layers, and other functional ceramics.

2. EXPERIMENTAL

2.1. Materials

Silicon wafers with thermally oxidized surface layers (Si/SiO_2) were purchased and cut into pieces of $1 \times 2\,cm^2$, which are used as substrates. The Si/SiO_2 wafers were ultrasonically cleaned in 0.1 M NaOH solution for 20 minutes, immersed into piranha solution (3 vol. of 95–98 wt.% H_2SO_4:1 vol. of 30 wt.% H_2O_2) for 20 minutes, rinsed with deionized water 4 times and dried in air. A Na-MMT clay (Cloisite® Na^+) was purchased from Southern Clay Products (Gonzales, Tex, USA). The 0.03 wt.% clay suspension (pH = 7.24) was prepared by stirring clays with magnet at 1000 rpm speed in deionized water for 20 minutes and then ultrasonicated for 20 minutes to achieve complete dispersion and exfoliation. Other chemicals were purchased from Sigma (Sigma-Aldrich, Saint Louis, MO, USA). Two different zirconium cationic precursor solutions were used to examine their suitability for growing the zirconia nanolayers on clay nanoplatelets, including 0.1 M zirconium chloride solution ($ZrCl_4$, pH = 1.32) prepared from zirconium

(IV) oxychloride octahydrate and zirconium acetate solution ($ZrAc_4$, pH = 4.14) prepared from zirconium (IV) acetate hydroxide. Sodium poly(styrenesulfonate) (PSS) and poly(ethyleneimine) (PEI) were dissolved in deionized water at concentrations of 1.5 mg/mL for the preparation of polymer-clay multilayers.

2.2. *Wet chemical synthesis and annealing*

Two steps were involved in the synthesis of oxide-clay multilayers: (1) wet chemical construction of multilayer precursors (termed as-deposited films), and (2) thermal dehydration and crystallization at elevated temperatures to form the annealed films. This preliminary study particularly focused on demonstrating the feasibility of the first step, which is more critical for developing the targeted clay-oxide multilayers. Thus the dehydration and thermal annealing conditions were preselected as a rule of thumb to be 600°C in air for 2 hours under 1 atmospheric pressure, since most MMTs can maintain their crystal structure intact (i.e., no dehydroxylation) below temperatures of 600–650°C. However, the control parameters of thermal annealing or hydrothermal treatment (i.e., the second step of synthesis) will be further optimized in future studies.

A computer-controlled programmable Nima dip coater (Nima Technology Ltd., Coventry, UK) was used to synthesize nanostructured as-deposited multilayers. To verify the LBL deposition method and the functions of the dip coater, nanoclay-polymer films were prepared following the recipe in Lvov et al. [17]. The Si/SiO_2 substrates were pretreated by dipping into PEI, PSS, and PEI solutions each for 20 minutes. The pretreated substrates were then dipped into a clay suspension for 20 minutes, rinsed with water for 2 minutes, dipped into a PEI solution for 20 minutes, and rinsed again with water for 2 minutes to complete one deposition cycle. This four-step deposition cycle was repeated 8 times to make nanoclay-polymer multilayers, denoted as (PEI-PSS-PEI)-$(MMT\text{-}PEI)_8$. Both the dipping and withdrawing speeds were controlled at 20 mm per minute.

To prepare nanoclay-oxide multilayers, the precleaned silicon substrates were dipped into a zirconium cationic precursor solution ($ZrCl_4$ or $ZrAc_4$) and the exfoliated nanoclay suspension alternately without interdipping rinsing. The deposition cycle was repeated 15 to 30 times to prepare the as-deposited multilayers. Both the dipping and withdrawing speeds were controlled at 20 mm per minute. The holding time was kept 45 seconds in air, Zr precursor solution and clay suspension. After completing a certain number (n) of deposition cycles, the substrates were then air-dried at room temperature to form the as-deposited films or annealed isothermally to 600°C for 2 hours to form the annealed films, denoted as $(\text{clay-oxide})_n$. A constant heating and cooling rate of 5°C per minute was used during annealing.

2.3. *Characterization*

Both as-deposited (i.e., air-dried) and annealed films were characterized by a Hitachi S4800 field-emission scanning electron microscope (FE-SEM) equipped with an energy dispersive X-ray spectroscopy (EDXS) analyzer. SEM specimens were coated with Pt/Au for increased conductivity. In addition, a Hitachi S3500 variable-pressure SEM was employed to examine specimens without conductive coating. Both in-plane and cross-sectional surfaces of the multilayers were studied. Fresh cross-sectional surfaces were created by carefully cleaving the Si wafers, while protecting the films with soft filter paper. Multiple measurements on different points were conducted to obtain the film thickness on cross-sectional surfaces under SEM. EDXS was also performed to analyze both qualitatively and quantitatively the elemental composition of the multilayers.

X-ray diffraction (XRD) was performed on both as-deposited and annealed films in a Scintag diffractometer using Cu-K_α radiation ($\lambda = 1.5418$ Å) generated at 40 kV and 35 A at a scan speed of 1°(2θ) per minute, step size of 0.01°, and a scan range of 1–60°2θ. In addition, a bare Si/SiO_2 substrate was scanned by XRD to examine any potential influence of the substrate on the observed diffraction patterns of the ultrathin multilayers.

3. RESULTS AND DISCUSSION

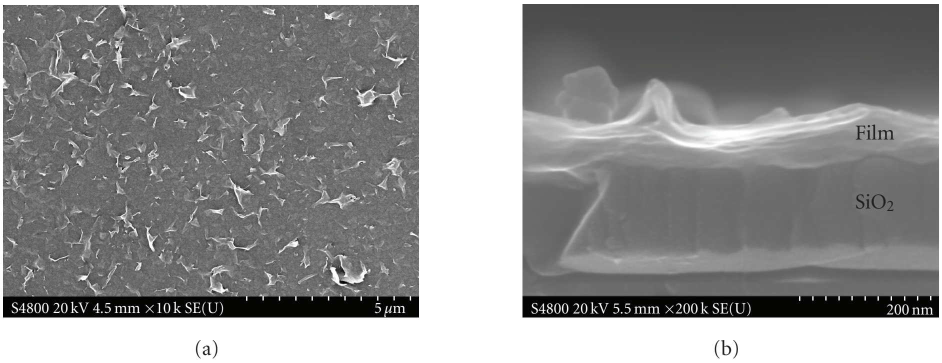
3.1. *Clay-polymer multilayers*

SEM images of the planar and cross-sectional surfaces of the as-deposited nanoclay-polymer multilayers [(PEI-PSS-PEI)-$(MMT\text{-}PEI)_8$] are shown in Figure 2. Some unevenly piled or protruded MMT platelets can be observed in the planar surfaces, as shown in Figure 2(a). The cross-sectional surface, as shown in Figure 2(b), exhibits nacre-like layered structure, which is similar to that observed in the films developed by Tang et al. [18]. The average measured film thickness is 40 ± 9 nm, of which 10 nm is from the precursor polymer film [17]. Thus the thickness of a single $(MMT\text{-}PEI)_1$ layer formed through a complete deposition cycle is approximately ∼3.75 nm, which is consistent with the previously reported value of 3.3 nm per deposition cycle [17]. It was postulated that the highly branched polycation PEI works as "electrostatic glue" [17] to assemble clay platelets. In conclusion, polymer-nanoclay multilayers with similar nanostructure were reproduced in our laboratory. This verified our equipment and procedures and enabled further exploration of synthesizing the new nanoclay-oxide multilayers.

3.2. *Clay-zirconia multilayers*

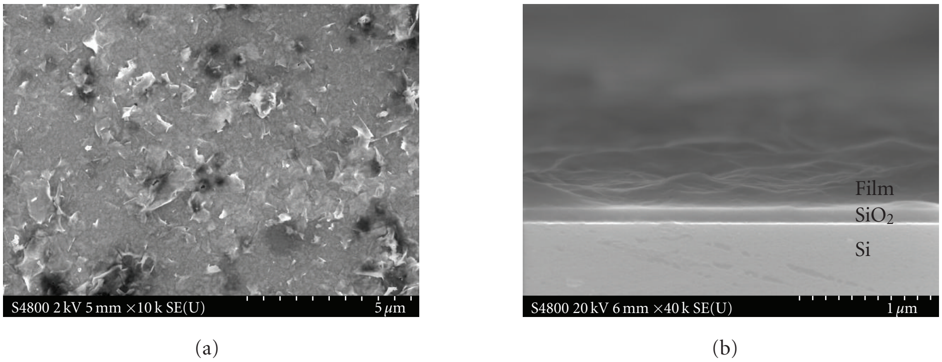
The SEM images of as-deposited films prepared by $ZrCl_4$ and $ZrAc_4$ cationic precursor solutions are shown in Figures 3 and 4, respectively. The as-deposited films were dried in air, thus either nanoclays or hydrated Zr cations are not completely dehydrated, and water molecules exist within the interface of clay nanoplatelets and Zr cations. Both films appear to be reasonably uniform and crack-free. Furthermore, they both exhibit observable layered structures in cross-sectional surfaces under SEM (Figures 3(b) and 4(b)).

Evidently, the films made by $ZrAc_4$ cationic precursor solutions have significantly smoother surface and more regularly (parallel) layered structure than those by $ZrCl_4$



(a) (b)

Figure 2: (a) Planar surface and (b) cross-sectional surface SEM images of as-deposited nanoclay-polymer [(PEI-PSS-PEI)-(nanoclay-PEI)$_8$] films.



(a) (b)

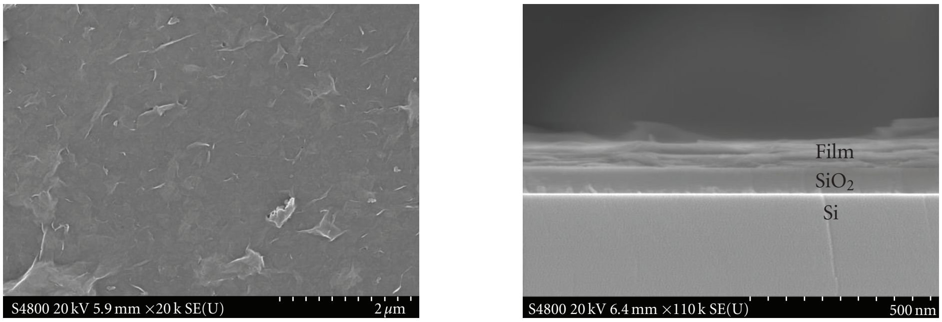
Figure 3: (a) Planar surface and (b) cross-sectional surface SEM images of as-deposited nanoclay-zirconia multilayers made via $ZrCl_4$ cationic solution.

precursor solutions (Figure 3 versus Figure 4). The clay nanoplatelets are better oriented in the films prepared by $ZrAc_4$ cationic solutions, while peeled and protruded edges of clay platelets are frequently observed in the $ZrCl_4$ prepared films, as shown in Figure 3(a). For films prepared by $ZrCl_4$ precursor solutions, the layered structure is less close-packed with occasional, sparsely distributed open voids, as shown in Figure 3(b). The nanoclay-oxide multilayers prepared using $ZrAc_4$ precursor solutions also appear to have lower surface roughness than those polymer-nanoclay multilayers prepared in this and prior [17] studies. Based on these results, $ZrAc_4$ cationic precursor solutions are used exclusively to make multilayers in further studies.

SEM images of the planar and cross-sectional surfaces of annealed films are shown in Figure 5. The annealed films appear to be denser and more uniform than the as-deposited ones. Some indications of the layered structure can be observed in the cross-sectional surfaces under SEM, as shown in Figures 5(a) and 5(b). It should be noted that the observed cross-sectional surfaces were influenced by the actual (somewhat random) cleaving process and hence the layered structure is not always clearly visible. The surfaces of annealed films, as shown in Figure 5(c) are also smoother than those of as-deposited films, as shown in Figure 4(a); yet, some clay nanoplatelets can still be seen in Figure 5(c).

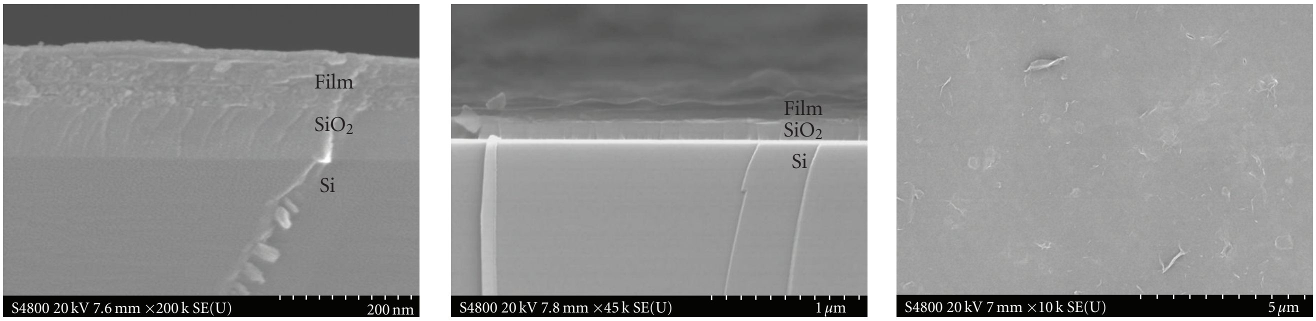
EDXS analysis of as-deposited and annealed films found the presence of Al, Si, and Zr, without other metal impurities. A representative EDXS spectrum is shown in Figure 6. Quantitative elemental analysis was also attempted with results shown in Table 1. We believe that the excess amounts of Si and O measured by EDXS are from the Si/SiO_2 substrates. Since the films are thin (less than 100 nm) and the penetration depth of an electron beam into a nonmetallic material is usually about 1 μm, the beam must be smeared. Although the quantitative compositional measurements are probably not accurate due to the beam spreading effect, it can be concluded that these films consist of oxides (or hydroxides) of Al, Si, and Zr without significant impurities of other elements.

XRD patterns of as-deposited and annealed multilayers are shown in Figure 7, in which the *d*-spacings are labeled for all peaks. As-deposited films appeared to be largely amorphous, but a series of low-angle peaks were observed. The 1.2 nm peak should result from hydrated montmorillonite, which usually exhibits the first peak (001) around 1.0–2.0 nm, depending on the degree of hydration (e.g., relative humidity) and the types of interlayer cations [19]. The as-deposited films were air-dried (i.e., the relative humidity is unknown) and contain Zr^{4+} as interlayer cations. Therefore, the montmorillonite in the air-dried films is likely to have a basal spacing of 1.2 nm. The presence of this peak indicates



(a) (b)

Figure 4: (a) Planar surface and (b) cross-sectional surface SEM images of as-deposited nanoclay-zirconia multilayers made by $ZrAc_4$ cationic solutions.



(a) (b) (c)

Figure 5: (a), (b) cross-sectional surface, and (c) planar surface SEM images of annealed nanoclay-zirconia films made by $ZrAc_4$ precursor solutions with 25 deposition cycles.

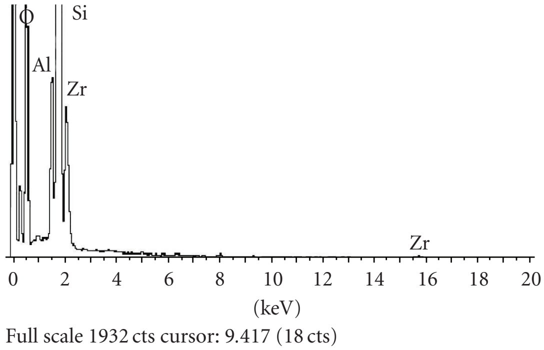


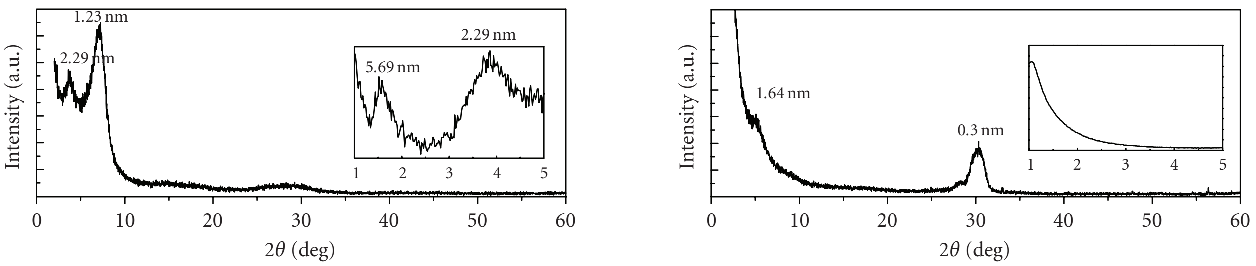
Figure 6: A representative EDXS spectrum for an annealed film.

Table 1: EDXS compositional analysis. Each value is the average of three measurements. The measured excessive amounts of Si and O are from Si/SiO_2 substrates, an artifact due to the spread of electron beams.

Element	Atomic %	
	As-deposited	Annealed
O	61.7	35.3
Al	3.6	1.2
Si	30.6	59.9
Zr	4	3.6

that some multiple layers of clay nanoplatelets are absorbed in dipping, which is not desired. The 5.7 nm peak represents the periodic thickness formed by each deposition cycle for the multilayers without annealing. The origin of the 2.3 nm peak is currently unclear and worth further investigation. It is noteworthy that the 1.2 nm peak is the sharpest of all peak, as shown in Figure 7(a). Given the low crystallinity of clay minerals, all other broad peaks suggest that the as-deposited multilayers possess much less ordered atomic structure or crystallinity, as expected. Nevertheless, a good layered nanostructure is clearly present in the as-deposited film with a periodic thickness of ~5.7 nm, as shown in Figure 7, indicating the success of the LBL deposition.

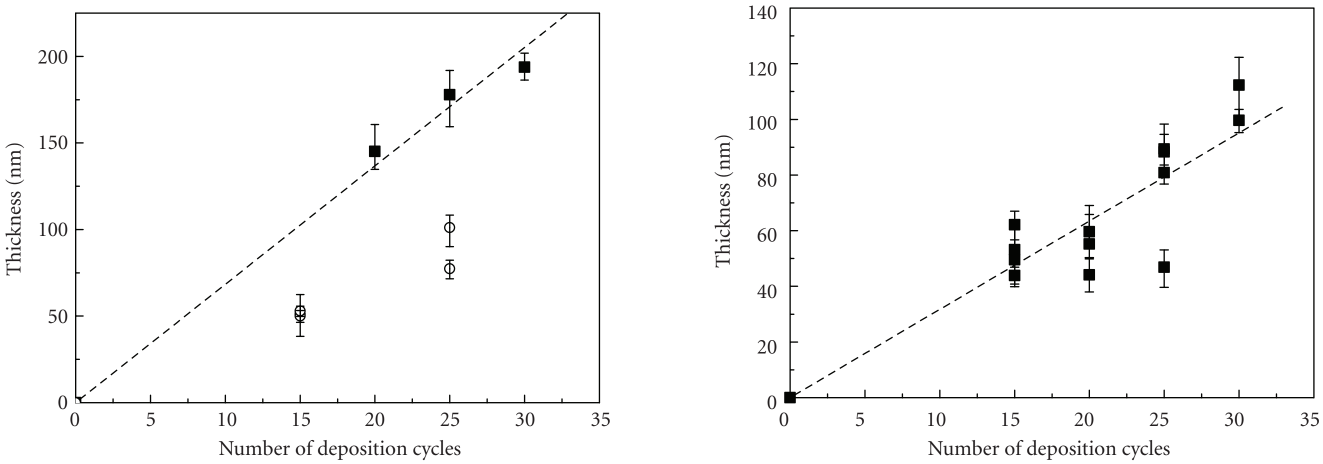
For annealed specimens Figure 7(b), only two peaks are observed. A broad weak peak at 1.6 nm is probably caused by the (002) reflection of the periodic thickness of 3.2 nm (see Section 3.3). The shape of the peak also indicates that the periodicity of the layers is not perfect, which is probably caused by the crystallization process during annealing. The low-angle scan did not find the (001) reflection at 3.2 nm, and the reason is unclear at present. The second peak at d = 0.3 nm matches ZrO_2 (111) reflection, indicating the formation of nanocrystalline ZrO_2. (It is noted that a broad weak peak whose intensity varies with the specific experimental



(a)

(b)

Figure 7: XRD patterns of (a) as-deposited and (b) annealed films formed by 20 deposition cycles and $ZrAc_4$ cationic solutions. The two XRD scans were carried out at the same conditions (scan rate and slit size) and the patterns are shown in the same intensity scale. The insets (which are shown in different intensity scales) are additional scans at low angles with a smaller slit.



(a)

(b)

Figure 8: Thickness versus the number of deposition cycles for (a) as-deposited and (b) annealed films made by $ZrAc_4$ precursor solutions. In (a), it is assumed that open circles represent measurement artifacts (as-deposited films where the part of layered films peeled off during cleaving of the substrates). Error bars represent the data range. Lines represent the best linear fits.

conditions was sometimes observed around 30° 2θ, which is believed to be caused by the Si/SiO_2 substrates [14, 15]. This is also seen in the XRD patterns of the as-deposited films, although a lower intensity was observed. Although these two measurements were made in the same conditions, it is still uncertain whether or not this peak at ∼30° 2θ is an artifact from the substrate). Assuming that this peak at ∼30° 2θ is indeed from ZrO_2 (111) reflection, the mean grain size of the nanocrystalline ZrO_2 was estimated to be ∼9.7 nm based on the peak width. Given that periodic thickness in the annealed film is approximately 3.2 nm (see Section 3.3), the ZrO_2 crystallite size of 9.7 nm indicates that the growth of nanocrystals may start to break the parallel multilayer structure (by displacing or heaving up nanoclay platelets which should act as barriers between two adjacent oxide layers), which is consistent with the absence of or week low-angle reflections from the annealed multilayers. Nonetheless, the existence of some layered structures is evident by SEM observations on the cross-sectional surfaces, as shown in Figures 5(b) and 5(c), but the layered structure is probably less regular, presumably due to the growth of ZrO_2 nanocrystals.

It is generally expected that montmorillonites are chemically stable for heating or annealing at 600°C [20]. More annealing experiments will be conducted to investigate how nanoclays react with Zr complexes during high temperatures, which will help form high temperature endurable nanoclay-oxide multilayers.

It is worth emphasizing that the annealed films still remained layered structure after cutting and no significant cracking or delaminating was observed in Figure 5, in spite of up to 50% linear shrinkage occurred during annealing, as discussed below.

3.3. *Film growth rate through LBL deposition*

The thickness of as-deposited and annealed films versus the number of deposition cycles prepared through $ZrAc_4$ cationic precursor solutions are shown in Figures 8(a) and 8(b), respectively. As-deposited multilayers are expected to exhibit low cohesion between layers, and part of the multilayers might fall off when they were cut along with the substrate for cross-sectional surface observations. This may be responsible for the measured unusually small thickness values (i.e., the three open circles shown in Figure 8(a)). If these data are excluded, the measured film thickness for both as-deposited and annealed films increase almost linearly with the number of deposition cycles. Through linear regression, the average film growth rates of as-deposited and annealed multilayers are ~6.8 nm and ~3.2 nm per cycle, respectively. In other words, annealing at 600°C for 2 hours caused a ~50% linear shrinkage of film thickness, which is nearly the same as that previously observed for pure ZrO_2 films [14, 15]. The shrinkage also indicates dehydration and sintering have occurred during annealing. The periodic layer spacing of the as-deposited multilayers was ~5.7 nm, as measured by XRD, as shown in Figure 7, which should be more accurate than the value (~6.8 nm) obtained by SEM measurement. However, the XRD and SEM measurements (5.7 nm versus 6.8 nm) are rather consistent.

3.4. *Issues, future studies, and potential applications*

As discussed above, the preliminary results are promising. However, the combined XRD, SEM, and EDXS characterization indicates that the multilayers synthesized in this study are not yet perfect, and there are some deviations from the targeted nanostructure shown in Figure 1(b). First, the 1.2 nm peak in XRD patterns in Figure 7(b) indicates that nanoclays are not completely exfoliated into single 2 : 1 layers and multiple layers of clay nanoplatelets are deposited within the films. This can be further improved by fine tuning the clay suspension chemistry, exfoliation method, and dipping process. Second, while as-deposited films exhibit fairly good layered structure, the thermally annealed films appear to possess relatively poor periodicity, as evident by both SEM and XRD. Annealing at 600°C for 2 hours in air was the only dehydration process that has been tested so far (since this study focused more on the feasibility of the LBL deposition). Further optimization of the annealing procedure will be conducted to identify optimal conditions based on a trade-off between dehydration and the structure integrity. Hydrothermal annealing [13] may be an alternative method to crystallize the oxides while maintaining the stability of clays and multilayered structure.

Nonetheless, this study has clearly demonstrated the basic feasibility of this new LBL technique for making this new class of nanostructured nanoclay-oxide multilayers. Further research should be conducted to finely tune the thickness and composition of each individual oxide layers (i.e., oxides other than ZrO_2) by changing the deposition parameters and precursor solutions, which offers significant versatility for making nanostructured films with diverse functionalities and applications.

The clay-oxide multilayers are expected to have many potential applications, which include but are not limited to coatings and free-standing membranes (made by using sacrificial substrates) for MEMS/NEMS and sensors. This is, in part, owing to the unique-layered nanostructure, as demonstrated by the organic-inorganic hybrid counterparts—nanoclay-polymer multilayers. In particular, a purely inorganic nanostructured composite consisting of zirconia and nanoclays has high thermal resistance (e.g., stable up to 800°C) and high hardness and is chemically inert. Thus, it can be used as protective and hard coatings. In addition to the high hardness of nanocrystalline ZrO_2, the presence of platy nanoclay layer within the structure increases fracture toughness by deflecting cracks, rendering even higher hardness of the multilayers. The high lateral bond strength of nanoclays ensures the integrity of free-standing films and membranes, and hence enhances the dynamic or vibrational performance. Potential applications in cantilever sensing components can be envisioned. Finally, it is expected that this purely inorganic nanostructured composite consisting of zirconia and nanoclays exhibits much higher thermal and chemical stability than their hybrid counterparts.

4. CONCLUSIONS

A novel layer-by-layer deposition technique has been developed for manufacturing nanoclay-zirconia multilayers by sequentially dipping a substrate in an exfoliated nanoclay suspension and a zirconia cationic precursor solution followed by annealing at 600°C for 2 hours. Nanoscale layer-by-layer growth is achievable, as evidenced by a linear film growth rate per deposition cycle measured on the cross-sectional surfaces under SEM and by X-ray diffraction. It is found that $ZrAc_4$ is a better cationic precursor solution for growing more uniformly layered films. The growth rate of as-deposited films is ~5.7 nm per cycle; the growth rate can be further tuned by changing the deposition parameters and dipping settings. Denser dehydrated films form after annealing at 600°C for 2 hours in air and the film thickness shrinks by ~50%; yet, the annealed films remain uniform and crack-free, and still possess nanoscale layered structure (although less clearly observable under SEM). In summary, the feasibility of the new LBL deposition technique has been clearly demonstrated, but the postdeposition dehydration and annealing processing should be further optimized.

The success of this study enables further endeavors to make a variety of novel oxide-based nanostructured films. This LBL deposition technique can be conveniently adapted for making periodic multilayers or functionally graded oxide films via changing the composition or concentration of oxide cationic precursor solutions periodically or continuously. Nanoclays with permanent surface charges are used to further assist electrostatic assembling, serve as diffusion barriers for functionally graded films, and incorporate other functional materials. It is expected that such purely inorganic nanostructured thin films exhibit unique mechanical properties, permeability, and corrosion resistance. Further research to optimize the synthesis methods (particularly the postdeposition dehydration process) and investigate their mechanical and physical properties is currently in progress.

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REFERENCES

[1] J. H. Fendler, “Self-assembled nanostructured materials,” *Chemistry of Materials*, vol. 8, no. 8, pp. 1616–1624, 1996.

[2] K. Ariga, Y. Lvov, I. Ichinose, and T. Kunitake, “Ultrathin films of inorganic materials (SiO_2 nanoparticle, montmorillonite microplate, and molybdenum oxide) prepared by alternate layer-by-layer assembly with organic polyions,” *Applied Clay Science*, vol. 15, no. 1-2, pp. 137–152, 1999.

[3] M. Isayama and T. Kunitake, “Self-supporting films of clay minerals and metal oxides: molecular ceramics,” *Advanced Materials*, vol. 6, no. 1, pp. 77–78, 1994.

[4] P. Podsiadlo, Z. Liu, D. Paterson, P. B. Messersmith, and N. A. Kotov, “Fusion of seashell nacre and marine bioadhesive analogs: high-strength nanocomposite by layer-by-layer assembly of clay and L-3,4-dihydroxyphenylalanine polymer,” *Advanced Materials*, vol. 19, no. 7, pp. 949–955, 2007.

[5] M. Rubner, “Materials science: synthetic sea shell,” *Nature*, vol. 423, no. 6943, pp. 925–926, 2003.

[6] Z. Tang, N. A. Kotov, S. Magonov, and B. Ozturk, “Nanostructured artificial nacre,” *Nature Materials*, vol. 2, no. 6, pp. 413–418, 2003.

[7] P. T. Hammond, “Form and function in multilayer assembly: new applications at the nanoscale,” *Advanced Materials*, vol. 16, no. 15, pp. 1271–1293, 2004.

[8] Y. F. Nicolau, “Solution deposition of thin solid compound films by a successive ionic-layer adsorption and reaction process,” *Applications of Surface Science*, vol. 22-23, pp. 1061–1074, 1985.

[9] T. P. Niesen and M. R. De Guire, “Review: deposition of ceramic thin films at low temperatures from aqueous solutions,” *Journal of Electroceramics*, vol. 6, no. 3, pp. 169–207, 2001.

[10] T. P. Niesen and M. R. De Guire, “Review: deposition of ceramic thin films at low temperatures from aqueous solutions,” *Solid State Ionics*, vol. 151, no. 1–4, pp. 61–68, 2002.

[11] Y. Aoki and T. Kunitake, “Solution-based fabrication of high-κ gate dielectrics for next-generation metal-oxide semiconductor transistors,” *Advanced Materials*, vol. 16, no. 2, pp. 118–123, 2004.

[12] Y. Aoki, T. Kunitake, and A. Nakao, “Sol-gel fabrication of dielectric HfO_2 nano-films; formation of uniform, void-free layers and their superior electrical properties,” *Chemistry of Materials*, vol. 17, no. 2, pp. 450–458, 2005.

[13] S. Park, B. L. Clark, D. A. Keszler, et al., “Low-temperature thin-film deposition and crystallization,” *Science*, vol. 297, no. 5578, p. 65, 2002.

[14] P. K. Arcot and J. Luo, “Layer-by-layer deposition of zirconia thin films from aqueous solutions,” *Materials Letters*, vol. 62, no. 1, pp. 117–120, 2008.

[15] P. K. Arcot and J. Luo, “Solution-based synthesis of oxide thin films via a layer-by-layer deposition method: feasibility and a phenomenological film growth model,” *Surface and Coatings Technology*, vol. 202, no. 12, pp. 2690–2697, 2008.

[16] N. A. Kotov, T. Haraszti, L. Turi, et al., “Mechanism of and defect formation in the self-assembly of polymeric polycation-montmorillonite ultrathin films,” *Journal of the American Chemical Society*, vol. 119, no. 29, pp. 6821–6832, 1997.

[17] Y. Lvov, K. Ariga, I. Ichinose, and T. Kunitake, “Formation of ultrathin multilayer and hydrated gel from montmorillonite and linear polycations,” *Langmuir*, vol. 12, no. 12, pp. 3038–3044, 1996.

[18] Z. Tang, N. A. Kotov, S. Magonov, and B. Ozturk, “Nanostructured artificial nacre,” *Nature Materials*, vol. 2, no. 6, pp. 413–418, 2003.

[19] G. Borchardt, *Minerals in Soil Enviroments*, SSSA Book Series 1, Soil Science Society of America, Madison, Wis, USA, 2nd edition, 1989.

[20] G. W. Brindley, “Invited review: ethylene glycol and glycerol complexes of smectites and vermiculite,” *Clay Minerals*, vol. 6, p. 273, 1966.