

Nanostructured Ceramic Film Formation on Self-Assembled Monolayers via a Biomimetic Approach

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ABSTRACT

A biomimetic approach is employed to deposit ceramic films on organic self-assembled monolayers (SAMs) coated substrates. Specifically, zirconia (ZrO_2) films are grown in a zirconium sulfate precursor solution at near room temperatures ($\sim 70^\circ\text{C}$). This process, directed by the nanoscale organic template, mimics the controlled nucleation and growth of the biominerals such as bones and teeth. The resultant zirconia films consist of nanosized particles (5-10 nm) that are precipitated out in a supersaturated precursor solution. Cross-sectional TEM and STEM works were performed to quantitatively analyze the film structure and chemistry, as well as interfacial region of the ceramic-SAM films. A stepwise deposition process was developed to avoid excessive formation of aggregation. Further, the dynamic nanoindentation testing was employed to assess the thickness and film-only intrinsic mechanical properties for direct comparison among the films processed with different processing parameters and microstructures. The films with finer particulate structure displayed higher intrinsic modulus than did those with coarser structure.

INTRODUCTION

Ceramic thin films have been suggested as a hermetic packaging alternative for microelectromechanical system (MEMS), microelectronics, and sensors in harsh and corrosive environments. A major challenge to produce ceramic thin films is to find a low-temperature synthetic route, as well as to possess microstructures that can accommodate the mechanical and thermal stresses. Interestingly, the best example of controlled ceramic formation is routinely observed in nature. A few specific examples include eggshells, teeth, bones, and kidney stones whose growth, morphology, and composition are directed by organic matrices.

In light of the natural biomineralization process, researchers have developed a promising biomimetic deposition approach in which self-assembled monolayers (SAMs) are employed as an organic template onto which ceramic thin films can be grown through hydrolysis of a precursor solution at near room temperature [1-3]. Thin films of ZrO_2 [3], Y_2O_3 -doped ZrO_2 [1], Y_2O_3 [4], SnO_2 [5], ZnO [6], TiO_2 [7], and V_2O_5 [8] have thus far been prepared using this technique.

In this study, zirconium oxide films were formed on the SAM-coated silicon wafers through the hydrolysis of zirconium sulfate ($\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$) solutions in acid environment at 70°C . One purpose of this study is to develop a bilayer structure that employs the advantages of organic SAM while processing hard and stiff ceramic protective films. We herein report the synthesis of the ZrO_2 /SAM bilayer films and corresponding nanostructure and mechanical properties.

EXPERIMENTAL PROCEDURE

The substrates used in this study were n-type (100) single crystal silicon wafers (Silicon Quest International, Santa Clara, CA). They were cut into ca. 1 cm x 1 cm samples. The silicon substrates were then sonicated in acetone, and then cleaned by freshly prepared piranha solution (1 part 30% H_2O_2 + 3 parts 98% H_2SO_4) for 30 min. The SAMs were then deposited on the hydrolyzed silicon substrates by immersion in a 1 vol% diethylphosphatoethyltriethoxysilane ($\text{C}_{12}\text{H}_{29}\text{O}_6\text{PSi}$; Gelest Inc., Morrisville, PA) anhydrous acetonitrile solution inside a nitrogen-filled glove bag at room temperature for 18 hours. The SAM-coated wafers were then sonicated with ethanol and dried completely with nitrogen gas. The SAMs were further hydrolyzed by immersing the substrates in 1 M HCl solution at 70°C in order to obtain a suitable surface terminus ($-\text{PO}(\text{OH})_2$) for the subsequent ZrO_2 deposition.

Ceramic deposition was carried out through a near-room temperature aqueous solution process. A freshly prepared 5 mM zirconium sulfate ($\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, Alfa Aesar, Ward Hill, MA) + 0.2~0.4 M HCl aqueous solution was used as a precursor solution. The substrates (SAM-coated silicon wafers) were stacked vertically in the precursor solution and kept in a constant temperature oil bath set at 70°C for 0.5~24 h. A stepwise deposition process was implemented by changing the precursor solution with the freshly prepared one every specified interval (1~2 h). After desired deposition steps and time were reached, the substrates were sonicated and rinsed with deionized water, and dried completely with nitrogen gas.

The nanostructure and chemical elemental distribution of the as-deposited ZrO_2 films were characterized by using cross-sectional transmission electron microscope (TEM, HF-2000, Hitachi) and scanning transmission electron microscope (STEM, HD-2000, Hitachi), respectively. Evolution of film morphology was examined using scanning electron microscope and optical microscope. Mechanical properties of the as-deposited films were characterized using nanoindentation with a built-in atomic force microscope (AFM) (TriboIndenter®, Hysitron Inc., Minneapolis, MN).

RESULTS AND DISCUSSION

The ceramic film formation can be achieved through two nucleation mechanisms: 1) heterogeneous nucleation at the interface between the substrate and solution, and 2) homogeneous nucleation by forming stable nuclei in a supersaturated solution. In the former mechanism, dissolved ionic species may attach to the SAM surface through an ion-by-ion growth mechanism. This is connected to directed growth of nuclei of the inorganic phase and formation of crystalline structures. Single crystal calcium carbonate has been synthesized in a similar mechanism [9]; however, little evidence of this mechanism was found for the deposition of ZrO_2 films in our study. In the latter mechanism, ZrO_2 crystals formed by homogeneous nucleation can form colloidal particles in solution and be attracted to the properly treated surface due to electrostatic and van der Waals interactions.

Our previous study [3] demonstrated that the as-deposited ZrO_2 films consist of tetragonal ZrO_2 crystallites in size of 5-10 nm. Orientations of the ZrO_2 crystallites near the $\text{ZrO}_2/\text{SAM-SiO}_2$ interfacial areas and across the film thickness direction were studied via cross-sectional TEM analyses. Figure 1 displays an example of crystal orientation of those nanocrystallites initially grown near the interface. No significant texture exists near the interfacial area or across the film thickness. This random orientation of the crystallites suggests the dependence of film

formation on the homogeneous nucleation mechanism. It should be noted that the cross-sectioned specimens were not thin enough to have only one layer of ZrO_2 crystallites for the determination of unambiguous crystal orientation; in fact, the cross-sectional TEM lattice images reflected the overlapping of a few layers of the ZrO_2 crystallites.

STEM analysis on the as-deposited ZrO_2 films revealed small amounts of sulfur (S), believed to be from the remaining amorphous zirconium sulfate that did not transform to ZrO_2 under the reaction regime proposed in Ref. [1]. In addition, non-uniform S distribution was observed near the interfaces. The STEM energy dispersive x-ray spectrometer (EDX) mapping exhibits the segregation of S on some areas where zirconium (Zr) is less populated, while Zr segregates to less S areas, as shown in Figure 2. These results are an indication of the presence of hydrolysis and condensation of sulfate products in lieu of the precipitation of an ionic salt.

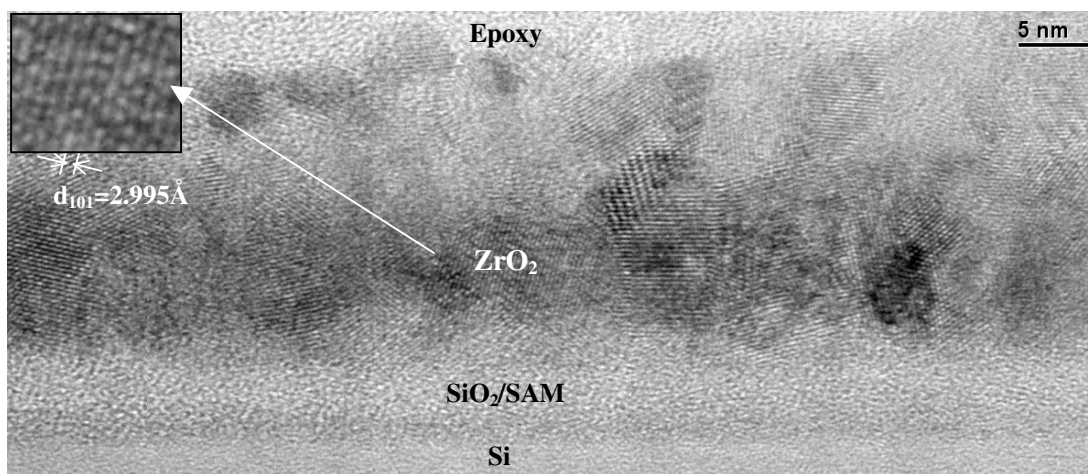


Figure 1. Cross-sectional TEM image of nanostructured ZrO_2 films at an early stage of the growth (thickness ≈ 23 nm) showing a quasi-random orientation of the crystals grown on SAM/Si. Inset: High resolution lattice image of the tetragonal ZrO_2 .

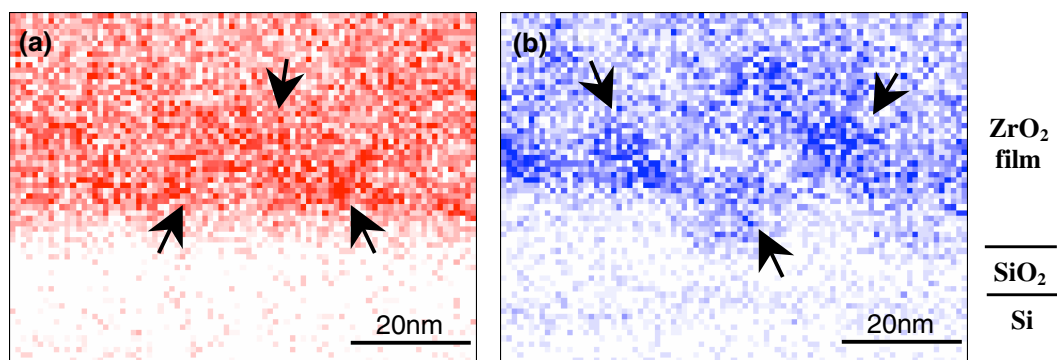


Figure 2. STEM EDX mapping on the interfacial area between Si/ SiO_2 and ZrO_2 films. (a) Zr map, with arrows indicating segregation of Zr; (b): S map, with arrows indicating segregation of S. It is noted that S is found more on the areas where Zr is less populated, and vice versa.

The ZrO_2 films deposited on SAM-coated silicon are free of crack if the films are thin enough, as shown in Figure 3 (a). However, as the films grew thicker, crack formation was observed and became more evident on thicker ZrO_2 films. Figure 3 (b) and (c) show the cracks on the as-deposited ZrO_2 films. Cracking of the film could be caused by volume changes during

drying [10]. It indicates that crack formation is more probable in places where the aggregates of the ZrO_2 particles are embedded in or adsorbed on the films.

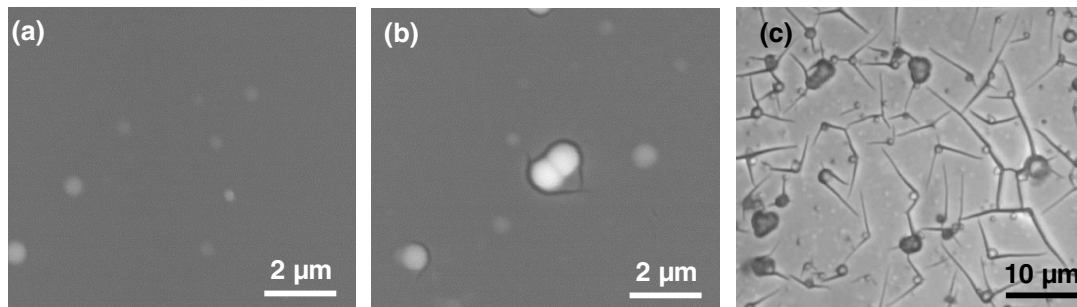


Figure 3. (a) An SEM image of as-deposited ZrO_2 film on SAM-coated silicon showing no apparent cracks (top view); (b) SEM image and (c) optical image of the ZrO_2 films with cracks. As shown, cracks are often initiated from the place where aggregates are embedded or adsorbed.

A stepwise deposition process was developed in an effort to avoid extensive bulk precipitation resulting from a long continuous immersion in the precursor solution, which could lead to the formation of surface aggregates in the film. In fact, extensive precipitation in solution occurred when the solution had been kept at 70 °C for 1 hr. Therefore, the precipitated solutions were changed with freshly-prepared ones every 1~1.5 hr, which reduced the aggregates in the films significantly. As shown in Figure 4, the stepwise deposition (1.5+1.5 hr) exhibited much more uniform, close-packed film structure, compared to that through the continuous deposition (3 hr). It is likely that there is less chance for crack formation under the stepwise deposition than under continuous deposition, due to the fact that fewer aggregates are adsorbed on the films under the former process.

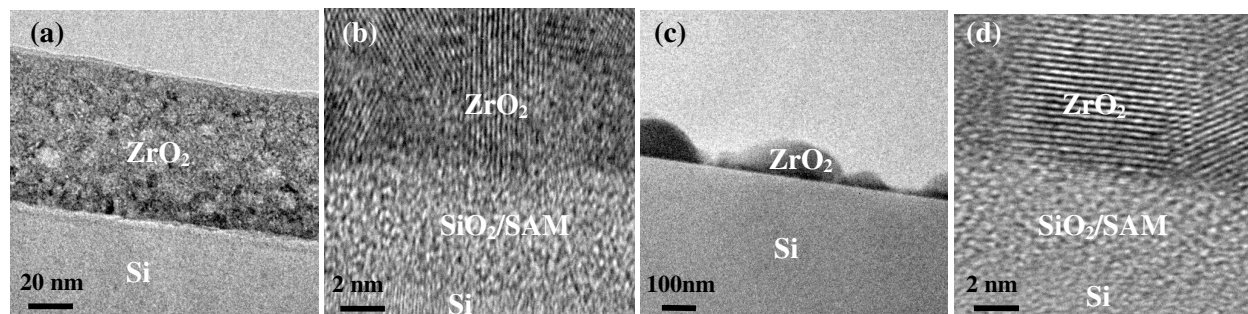


Figure 4. Cross-sectional TEM images of nanostructured ZrO_2 films grown on SAM-coated Si in solution: (a) after stepwise 1.5+1.5 hr deposition; (b) higher magnification of the film-substrate interface of (a); (c) after continuous 3-hr deposition; (d) higher magnification of the film-substrate interface of (c).

Mechanical properties of the as-deposited ZrO_2 films were studied using nanoindentation. The indentation response of a thin film on a substrate is a complex function of the elastic and plastic properties of both the film and substrate. Numerous models have been proposed in order to isolate the ‘film-only’ properties from the substrate effect. In this study, based on Saha and Nix’s model [11], we developed a method using dynamic nanoindentation to measure the intrinsic modulus (E_f) and the thickness of the ceramic thin films, by applying non-linear curve fitting on the reduced modulus as a function of indenter displacement obtained from a single

dynamic indentation [12]. Figure 5 shows an example of the curve fitting. The reduced modulus of the films increases continuously as the indenter approaches to the substrate. The point at which the extrapolated reduced modulus of the film reaches that of silicon substrate (~ 154 GPa) corresponds to the film/substrate interface.

The results showed that the film thicknesses estimated by this method were consistent with those by atomic force microscope (AFM) cross-sectional profile [12]. The average intrinsic modulus of the as-deposited ZrO_2 films was found to be 15.7 ± 4.5 GPa, which was also consistent with that obtained from quasi-static nanoindentations [13]. It was found that intrinsic modulus was independent on indentation depth. We also found that this method can be applied to thin films deposited on a more compliant substrate, e.g., ZrO_2 films on polymer substrate [12].

Intrinsic moduli of two films with significantly different structures were characterized and compared, as shown in Figure 6. It was found that the film with finer particulate structure (i.e., clustered nanoparticles) exhibited higher intrinsic modulus (Figure 6a, RMS roughness=17 nm, $E_f=19.6$ GPa) than did that with coarser structure (Figure 6b, RMS roughness=33 nm, $E_f=15.3$ GPa).

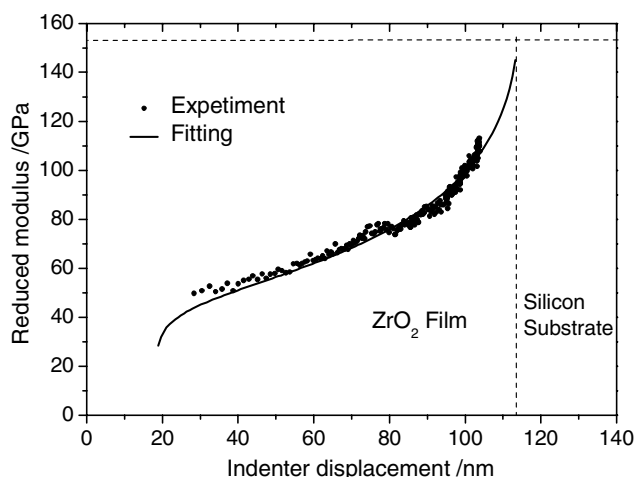


Figure 5. Non-linear curve fitting on reduced modulus vs. indenter displacement, for the determination of intrinsic modulus and film thickness.

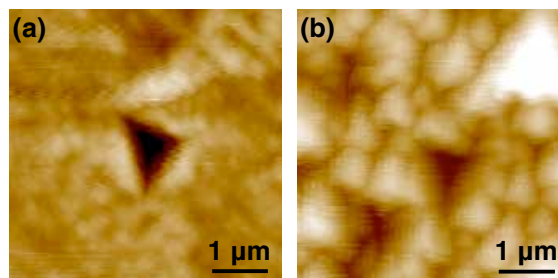


Figure 6. AFM images showing the nanoindentations made on two different films with (a) finer structure and (b) coarser structure.

CONCLUSIONS

Nanostructured ZrO_2 thin films were deposited on silicon substrates in zirconium sulfate/HCl solutions at very low temperature (70°C) with the aid of self-assembled monolayers (SAMs). The nanocrystallites of tetragonal ZrO_2 near the film/substrate interface exhibited a quasi-random orientation. Small amount of sulfur exists in the as-deposited ZrO_2 film. Sulfur was not uniformly distributed, and was concentrated on the areas where zirconium was less populated. The as-deposited ZrO_2 films were free of cracks if films were thinner than a certain thickness, depending on the deposition process. Cracks, however, occurred as the films grew thicker. It appeared that cracks tend to nucleate at the places where the aggregates are embedded. Hence, a stepwise deposition process was developed in an effort to mitigate the extensive surface

aggregation under continuous deposition and therefore inhibit the crack formation in the as-deposited films.

Mechanical properties of the ceramic thin films were studied via nanoindentation. In order to compare intrinsic properties of the films, we have developed a method using dynamic nanoindentation to assess the substrate effect by applying non-linear curve fitting on the reduced modulus versus indenter displacement obtained from a single dynamic indentation. In this way, it was possible to evaluate the ‘film-only’ modulus as well as the thickness of the ceramic thin films. The results showed that the average intrinsic modulus of the as-deposited ZrO₂ films was 15.7 ± 4.5 GPa. The ZrO₂ films with finer structure exhibited higher intrinsic modulus than did those with coarser structure. It suggests a potential for further enhancement of mechanical properties by tailoring the microstructures.

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