SYNTHESIS AND PROCESSING OF NANOSTRUCTUERD CERAMIC THIN FILMS GROWN ON SELF-ASSEMBLED ORGANIC MOLECULES

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ABSTRACT

An aqueous solution processing route is employed to grow ceramic films on organic self-assembled monolayer (SAM) coated substrates. Specifically, zirconia (ZrO_2) films are grown from a precursor solution of zirconium sulfate at near room temperatures (70˚C). This process, directed by the organic template, mimics the controlled nucleation and growth of the biominerals such as bones and teeth. The resultant zirconia films consist of nanocrystallites (about 5-10 nm in diameter) that are precipitated out in a supersaturated solution and adhered to the substrate. The underlying mechanisms of generating the nanostructured films are systematically studied by tailoring solution chemistry and SAM functionalities. Cross-sectional, high-resolution TEM work is performed to quantitatively analyze the film structure and chemistry, as well as the interfacial region of the ceramic films near the SAM. In addition, the dynamic nanoindentation testing is developed to assess the intrinsic mechanical properties of the films processed with different processing parameters and microstructures. Adhesion of the films is characterized using a scratch test. This ceramic film growth mechanism can be sufficiently general that it may be applicable to other oxide systems.

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 biomimetic deposition approach in which self-assembled monolayers (SAMs) are employed as an organic template onto which ceramic thin films are grown through hydrolysis of a precursor solution at near room temperatures.[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 ($Zr(SO_4)_2 \cdot 4H_2O$) 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 and process optimization of the ZrO_2/SAM bilayer films, the corresponding nanostructures and mechanical properties, and the relationship between structures and 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 1cm x 1cm samples. The silicon substrates were sonicated in acetone, and then cleaned and activated by freshly prepared piranha solution (1 part 30% H_2O_2 + 3 parts 98% H_2SO_4) at ~80˚C for 30 min. The SAMs were then deposited on the activated silicon substrates by immersion in a 1 vol% diethylphosphatoethyltriethoxysilane ($C_{12}H_{29}O_6PSi$; 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 treated by immersing the substrates in 1 M HCl solution at 70˚C for 30 - 60 min in order to obtain a suitable surface terminus (-$PO(OH)_2$) 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 ($Zr(SO_4)_2 \cdot 4H_2O$, 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 held vertically or upside-down 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 the desired deposition steps and time were reached, the substrates were sonicated, rinsed with deionized water, and dried completely with nitrogen gas.

The nanostructure and elemental distribution of the as-deposited ZrO_2 films were characterized by using analytical transmission electron microscope (TEM, HF-2000, Hitachi) equipped with an energy dispersive x-ray spectrometer (EDS). 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 in aqueous solution 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. These mechanisms have been considered for the deposition of ZrO_2 films by immersing a SAM-coated substrate in a precursor solution of zirconium sulfate. 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 using a similar mechanism;[9] however, little evidence of this mechanism was found for the deposition of ZrO_2 films in our study as explained in the following paragraph. In the latter mechanism, ZrO_2 crystals precipitated out in solution create colloidal particles that are 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 of 5-10 nm in size. Orientations of the ZrO_2 crystallites near the ZrO_2/SAM-SiO_2 interfacial areas and across the film thickness direction were studied via cross-sectional TEM analyses. Figure 1 displays examples of crystal orientation of those nanocrystallites grown

near the interface and across the film thickness direction. 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.
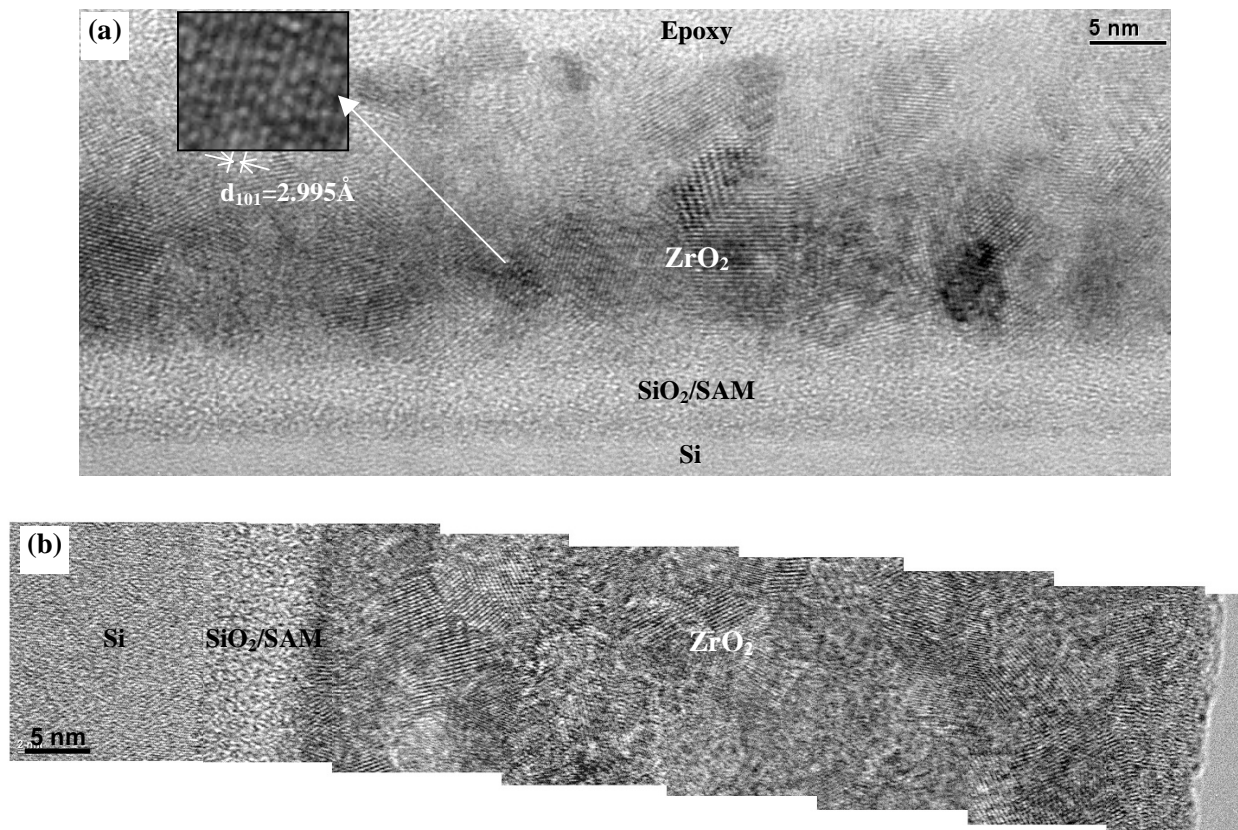

Figure 1. Cross-sectional TEM images of nanostructured ZrO_2 films (a) at an early stage of the growth (thickness=23 nm) and (b) with deposition of 3 hr (thickness=71 nm), both showing a quasi-random orientation of the crystals grown on SAM/Si. Inset of (a) shows a high-resolution lattice image of the tetragonal ZrO_2.

EDS 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 by Agarwal *et al.*[1] Pockets of sulfur segregation were found near the interfacial area. In addition, the Zr:S intensity ratio at the film/substrate interfacial area (~12:1) was higher by a factor of ~2 than that at the place far from interface (~6:1), suggesting a possible change in solution chemistry between the initial and subsequent film deposition.

The ZrO_2 films deposited on SAM-coated silicon are free of cracking if the films are thin enough, as shown in Fig. 2 (a). However, as the films grew thicker, crack formation occurred and became more evident on thicker ZrO_2 films. Figures 2 (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. The presence of particle aggregates on the

films can possibly be related to the conditions of the surface (SAM) as well as the precursor solution.
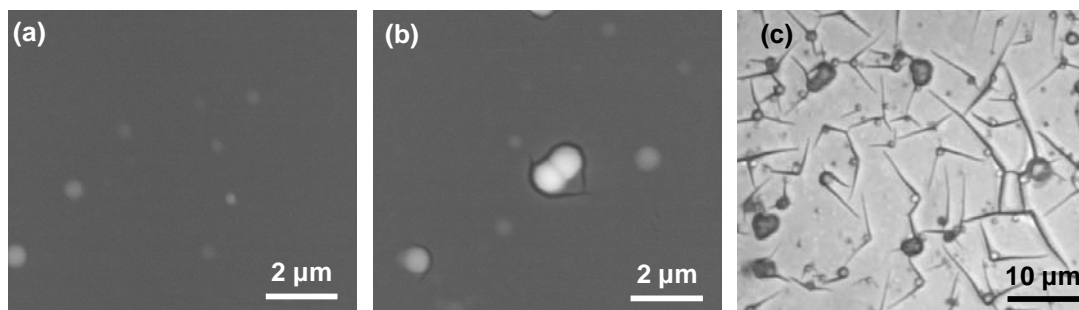

Figure 2. (a) An SEM image of as-deposited ZrO_2 film on SAM-coated silicon showing no apparent cracks (top view); (b) SEM image and (c) optical image of the ZrO_2 films with cracks. As shown, cracks are often initiated from the place where aggregates are embedded or adsorbed.

The 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 on 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 exchanged with freshly prepared ones every 1-1.5 hr, which reduced the aggregates in the films significantly. As shown in Fig. 3, the stepwise deposition (1.5+1.5 hr) exhibited a more uniform and dense film structure, compared to that processed through the continuous deposition (3 hr). It is likely that there is less chance of 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.
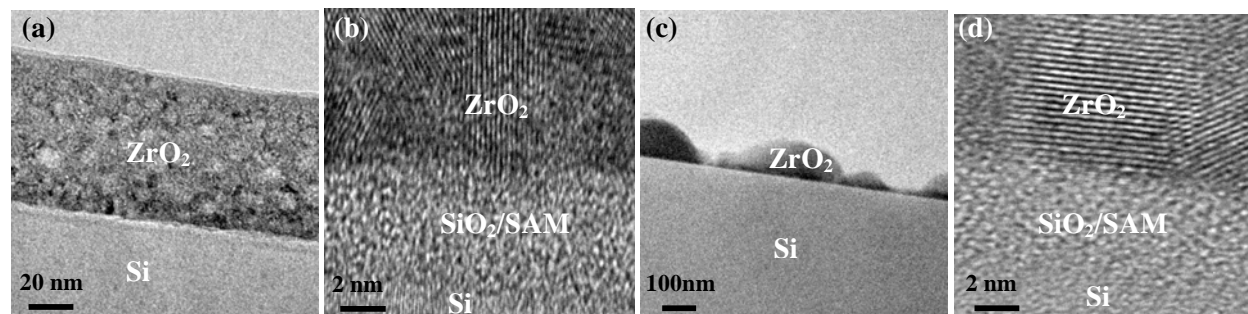

Figure 3. Cross-sectional TEM images of nanostructured ZrO_2 film grown on SAM-coated Si in solution: (a) after stepwise 1.5+1.5 hr deposition; (b) higher magnification of the film-substrate interface of (a); (c) after continuous 3 hr deposition; (d) higher magnification of the film-substrate interface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

For the samples held vertically during deposition, it was often found that the lower part of the film was more uniform than the higher part. This might be due to the difference in the flow pattern of the precursor solution at different elevations, since the flow pattern is a complex function of factors such as solution rheology, presence of stirring, and shape of the sample holder. In an attempt to deposit more uniform microstructures on a wide area, we also tried holding the substrates upside down in the precursor solution. The effect of upside-down orientation on the microstructure of the ceramic films is still under investigation.

Mechanical properties of the as-deposited ZrO_2 films were studied using nanoindentation. The indentation response of a thin film on a substrate is affected by elastic and plastic properties of the substrate, as well as those of the film. Numerous models have been proposed in order to isolate the 'film-only' properties from such a 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 indentation displacement obtained from a single dynamic indentation.[12]

In this model, the reduced modulus of the softer films increases continuously as the indenter approaches to the stiffer substrate. The point at which the extrapolated reduced modulus of the film reaches that of the substrate corresponds to the film/substrate interface. Our previous results on ZrO_2 films on a silicon substrate showed that the film thicknesses estimated by this method were consistent with those by an atomic force microscope (AFM) cross-sectional profile.[12] The intrinsic modulus of the ZrO_2 films was also consistent with that obtained from quasi-static nanoindentations.[13] The average modulus of the currently processed ZrO_2 films is 15.7 ± 4.5 GPa, and further work is in progress to enhance the properties. It was also found that intrinsic modulus was independent on indentation depth.

Using this method, the microstructural effect on the intrinsic modulus was investigated. Two types of films with significantly different structures were characterized and compared. It was shown that the film with finer particulate structure (i.e., consisting of clustered nanoparticles) exhibited higher intrinsic modulus (Figure 4 (a), RMS roughness=17 nm, E_f=19.6 GPa) than did that with coarser structure (Fig. 4 (b), RMS roughness=33 nm, E_f=15.3 GPa).
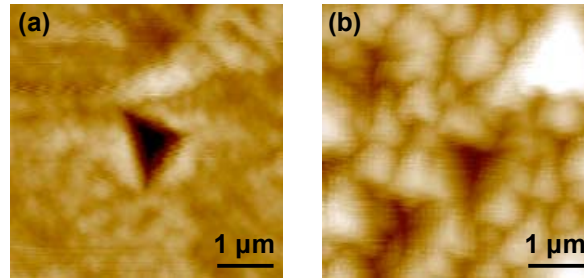

Figure 4. AFM images showing the nanoindentations made on two different films with (a) finer structure and (b) coarser structure.

Scratch tests using a lateral motion of a nanoindenter were employed to examine the adhesion of the aforementioned ZrO_2 thin films to the substrate. A maximum normal force in the range of 1000-2800 µN with a lateral displacement of 4 µm was applied to the films. Film delamination results in the abrupt change in friction coefficient, and the interfacial adhesion in terms of work (W_A) can be calculated as

$$W_A = \frac{t}{2E_f}\left(\frac{2P_{cr}}{\pi R^2}\right)^2 \quad , \tag{1}$$

where t is the film thickness, P_{cr} is the critical normal force when delamination occurs, and R is the radius of curvature of the indenter tip.[14] The interfacial adhesion of the ZrO_2 films with stepwise deposition on silicon substrate (Fig. 5 (a)) was measured to be 26.7 ± 3.0 J/m^2, which was much higher than that (1.4 J/m^2) of the films processed without stepwise deposition and thus exhibiting coarser and non-uniform microstructure (Fig. 5 (b)).
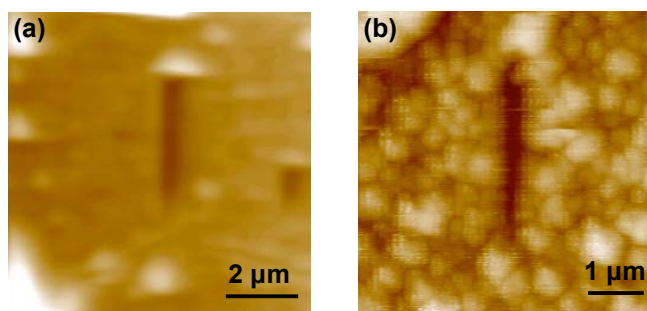
Figure 5. AFM images showing the scratches made on two different films with (a) finer structure and (b) coarser structure.

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. A small amount of sulfur exists in the as-deposited ZrO_2 film. Sulfur was not uniformly distributed, and was less concentrated at the interfacial area than far away from the interface. The as-deposited ZrO_2 films were free of cracks if films were thinner than a certain thickness, which depends on the deposition process. Cracks, however, occurred as the films grew thicker. It appeared that cracks tended to nucleate at locations where the aggregates were 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 and their relation to microstructures were studied via nanoindentation and AFM. 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. From the scratch test, interfacial adhesion was measured. The average intrinsic modulus of the as-deposited ZrO_2 films was 15.7 ± 4.5 GPa, and the average interfacial adhesion of the ZrO_2 films on silicon substrate was 26.7 ± 3.0 J/m^2. The ZrO_2 films with finer particulate structure exhibited a higher intrinsic modulus and better adhesion than did those with coarser structure. This suggests a great potential for further enhancement of mechanical properties by tailoring the microstructures.

ACKNOWLEDGMENTS

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