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Recommended Citation

Novel yttrium-stabilized zirconia polymeric precursor for the fabrication of thin films

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An acetate-based polymeric precursor for producing yttrium-stabilized zirconia (YSZ) was developed. The precursor was prepared under ambient conditions and contains only yttrium and zirconium cations. Dense, crack-free films were fabricated with this precursor on alumina substrates at a rate of 60 nm per deposition, producing polycrystalline YSZ at temperatures as low as 600 °C. Grain growth in thin YSZ films followed Arrhenius equation with an activation energy approximately 0.45 eV. The residual strain in YSZ films decreased with increasing annealing temperature from 600 to 900 °C.

I. INTRODUCTION

Thin film technology, a process that produces coatings less than 1 μm thick, is used extensively to fabricate such items as microelectronic[1] and piezoelectric[2] devices, insulate high temperature parts as thermal-barrier coatings,[3] generate wear resistant coatings,[4] or produce solid-oxide fuel cells.[5,6]

Thin films can be deposited by a number of techniques. Some techniques, such as sputtering[7] and ion plating,[8] use vacuum deposition. Sputtering uses high voltages to produce plasma around a solid target in a high vacuum. Ions from the target are then deposited onto a grounded substrate. Ion plating uses a vapor phase created by evaporation in a vacuum. The source is heated with an electron beam in a vacuum until a sufficiently high vapor pressure is achieved to cause the material to condense on a nearby substrate. Chemical vapor deposition (CVD)[9] produces a solid material on the surface of a heated substrate through a chemical reaction in the gas phase caused by heating a solid, liquid, or gas.

Wet-chemical processes are also used to produce films. In these processes, chemical solution is produced, containing the desired cations in the desired ratios along with a large amount of organic species. The organics in the solution serve as a backbone to keep the cations in a homogenous solution and to help control viscosity.[10] This solution is either then spun onto a substrate, known as spin-coating,[11] or the substrate is dipped into the solution, referred to as dip-coating.[11]

When producing films with multiple cations, wet-chemistry techniques use a chemical solution in which stoichiometry can be controlled, and thus tend to produce homogenous coatings. Vacuum deposition techniques require evaporation of a source. Evaporating multiple cations simultaneously is complex since the rate of evaporation for the different cations may not be the same under a given set of conditions, making control of the stoichiometry difficult.

Wet-chemistry based processes can take a variety of forms. Sol-gels[10] are often associated with thin films. A sol-gel is produced by first generating a stable colloidal solution, or sol, of metal or metalloid cations surrounded by various ligands in a solvent. Additional monomer species are then added to initiate the gel, or gelation step, which is marked by a significant increase in viscosity. The solvent is then evaporated, the organic species are removed by pyrolysis, and the result is a dense ceramic material.

Polymeric precursors[6,12] are an alternative to sol-gels. Polymeric precursors are produced by combining metal and metalloid cations much the same way as a sol. However, they are combined with weak organic acids and a polyhydroxyl alcohol, such as ethylene glycol, which act as chelation agents.[13] These serve to hold the cations in solution and control viscosity. Unlike sol-gels, polymeric precursors have no distinct gelation step.

Yttrium-stabilized zirconia (YSZ) thin films have been made with a number of techniques. Peshev et al.[14] used zirconium containing alcohols such as zirconium (IV) propoxide combined with yttrium (III) isopropoxide to produce good-quality YSZ films, but synthesis of the solution is highly sensitive to water and thus must be produced in a dry box under argon.

Not all systems require such strict processing environments; Gorman et al.[6] described a system consisting of zirconium oxychloride and yttrium nitrate. While this solution can be produced under ambient conditions, it is possible that some amount of chlorine will remain in the final film. Chlorine has a negative effect on both the

densification and the electronic resistivity of bulk YSZ. Quantities as small as 0.75 wt% chlorine can reduce the density of YSZ to 91% theoretical,[15,16] while the electronic resistivity can be lowered by as much as three orders of magnitude.[17] Commercial zirconia powders are often produced from zirconium oxychloride, and are subsequently washed to remove the chlorine.[15,16]

Zirconium acetate has been investigated as a source for zirconia precursors to produce pure, high quality powders[18,19] and thin films.[19] This acetate system does not contain any undesirable constituents that would survive pyrolization and does not require strict control of the environment.

In this investigation, the feasibility of producing quality YSZ thin films from a polymeric precursor of zirconium acetate and yttrium acetate was explored. The films produced were then characterized with various qualitative techniques to determine the quality and morphology of the films.

II. EXPERIMENTAL PROCEDURE

A. Polymeric precursor preparation

The overall process for fabricating the polymeric precursor and producing thin films is shown in Fig. 1. A polymeric precursor for producing ZrO_2:16% Y YSZ films was prepared by combining zirconium acetate, yttrium acetate, and ethylene glycol. The zirconium acetate solution was obtained from Aldrich (Milwaukee, WI) and used as received. An yttrium acetate solution was prepared by dissolving yttrium acetate (Aldrich) in distilled water while heating and stirring at 80 °C; undissolved species were minimized with vacuum filtration through 1-μm filter paper. The cation concentration of both solutions was determined by thermogravimetric standardization, where a known amount of solution was heated in an alumina crucible to 1000 °C, and the remaining oxide produced was measured. Ethylene glycol (Fisher, Pittsburgh, PA) was added to a mixture of zirconium and yttrium acetate stirring in a beaker on a 50 ± 10 °C hotplate. If the precursor is heated too quickly, precipitates will develop. At the point where the volume remained stable and solvent evaporation had ceased, after about 30 h, methanol was added to the solution to achieve the desired viscosity of approximately 20 ± 5 cP (as measured by a Viscolab 400 viscometer at 25 °C). This viscosity was found to produce the best films under the spin-coating conditions used. The resulting solution was clear and colorless. Filtration of the solution with a 0.45-μm glass fiber filter (Whatman, Inc., Clifton, NJ) minimized foreign material in the precursor. Solution concentrations were reported as a ratio of the total moles of cations to moles of ethylene glycol. One goal of this project was to maximize the cation concentration while still producing dense, crack-free films. Solutions containing
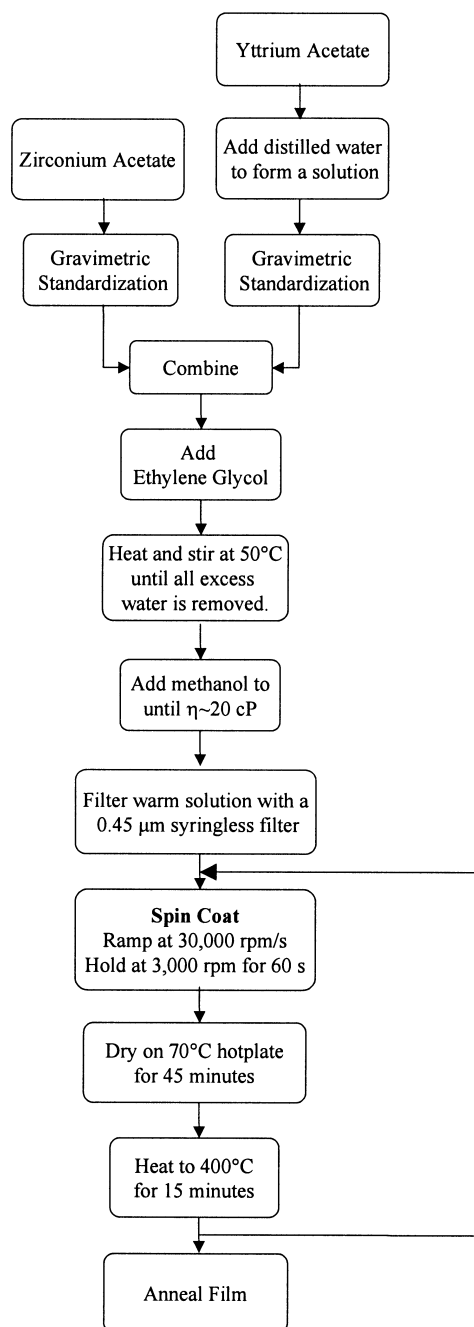

FIG. 1. Precursor preparation flow chart.

cation concentrations of 0.05:1, 0.10:1, and 0.25:1 (hereon referred to as 5%, 10%, and 25%) were investigated.

The rheology of the polymeric precursor was determined with a Haake VT500 (Haake, Germany) viscometer using a NV rotor. Thermogravimetric differential thermal analysis (TG/DTA) was performed with a Netzsch (Netzsch, Germany) STA409C.

B. Film deposition and crystallization

Thin films of YSZ were deposited on single-crystal alumina substrates (Kyocera), measuring one inch by one

inch, by spin coating (Brewer Science Model CEE100, MO). The substrates were cleaned prior to use by rinsing with ethanol and heating to 400 °C to minimize the presence of foreign organic material. An excessive amount of YSZ precursor, 10 drops, was deposited on the substrate by a pipette, and then spun at a rate of 3000 rpm for 60 s. The spin-coating program was chosen at the beginning of the project and all other relevant factors were tailored accordingly. Based on the results of a TG/DTA analysis performed on the precursor, the substrate was then cured at 70 °C for 0.75 h to slowly remove the solvents, and then immediately moved to a 400 °C hotplate for 0.25 h to minimize the organic species in the film. At this temperature, x-ray diffraction (XRD) analysis indicates that the precursor is still amorphous, although the extent of crystallization may have been impossible to detect. Additional depositions and heat treatments were then made until the desired thickness of 150 nm was reached. The film was then annealed on a zirconia setter plate for 1 h in an oven at temperatures ranging from 500 to 1200 °C for the purpose of examining grain growth.

The thickness and morphology of the final annealed films were analyzed by several techniques. The samples were imaged using a Hitachi (Tokyo, Japan) S-4700 Field Emission scanning electron microscopy (SEM). Atomic force microscopy (AFM, Digital Instruments, NY) analysis was performed with a Nanoscope IIIA Scanning Probe Microscope in tapping mode, and XRD (Panalytical, The Netherlands) was performed with a Phillips X-Pert MRD Diffractometer using Cu K_α radiation. Grain size analysis was performed on SEM and AFM results with Scion Image (Frederick, MD) 3b software.

III. RESULTS AND DISCUSSION

A. Precursor characterization

The technique used to produce this precursor differs greatly with the methods discussed earlier. The constituents are nonreactive with the atmosphere, thus reaction inside a dry box is unnecessary. There are no extra cations contained in this precursor that could be left in the final product other than yttrium and zirconium. Synthesis of this precursor is simple; all of the constituents are soluble in water.

Yttrium acetate has a solubility limit of approximately 8 wt% in water while zirconium acetate is about 53 wt%. Hence, if a solution were produced with only these two constituents, yttrium would precipitate after evaporating only 10% of the water in the system. By adding ethylene glycol, the system is changed in such a way as to prevent precipitation regardless of water loss and allowing for viscosities as high as 200 cP. There are a number of possible explanations for this effect, ranging from very simple to very complex. One of the more complex explanation is that the system may have chelated, an event

in which a system of organic rings surrounding metal ions develop in a solution, preventing precipitation.[13,20] A previous study by Pennell[21] describes how ethylene glycol is oxidized to form oxalic acid, a known chelation agent. Studies have been performed by other researchers indicating that the acetate group also acts as a chelation agent.[20,22] However, there are no agents present in this system to facilitate the oxidation of ethylene glycol, and the acetate group alone cannot cause chelation. A simpler possibility is that ethylene glycol has changed the solubility of the cations in solution and aids in controlling viscosity. Additional studies are required to clearly understand the exact nature of the reactions that take place in this system.

A series of experiments were performed in which the cation concentration of the polymeric precursor was varied and revealed that the maximum ratio of moles of cations to moles of ethylene glycol is approximately 25%. Precursors of higher concentrations suffered from visible precipitation during the initial heating.

For the range of cation concentrations investigated, the final precursor always had a pH of 4. Any attempt to vary this pH by as much as one in either the acidic or basic directions resulted in immediate gellation, thus any agent used to dilute the system must not change its pH.

This polymeric precursor does appear to suffer from an aging effect. Solutions that were allowed to sit dormant with water that was not chemically bonded began to age, resulting in visible precipitation. This effect is magnified as the cation concentration of the solution is increased. Removing the excess water from the solution can significantly slow this effect. The solution must be heated and stirred at 50 °C until no more weight loss occurs, and then diluted with an alcohol such as methanol to obtain the desired viscosity. This step has no effect on the final film quality.

Often a precursor will not sufficiently wet a substrate to produce a film, requiring additional wetting agents. For instance, YSZ precursors based on zirconium oxychloride require a 50/50 mixture with butoxy ethanol to facilitate wetting to produce dense films. The acetate-based precursor does not require any such agents in conjunction with the substrates used in this study. The wetting angle of the precursor was measured and found to be approximately 30° on Al_2O_3.

The final film thickness is significantly influenced by two separate properties of the precursor, viscosity and cation concentration. Rheology measurements indicate that this system exhibits Newtonian behavior, which is important for film thickness uniformity. The equations that describe spin-coating require that the precursor be insensitive to shear.[11] Under the spin-coating conditions used, precursors with a viscosity of 40 cP produced films that were 85 nm thick in the center but tapered off to 45 nm thick near the edge of the substrate per deposition.

This was caused by the initiation of solvent evaporation prior to the completion of a uniform film, and could be avoided by increasing the spin rate from 3000 to 4000 rpm. The estimated spin rate is based on

$$q \propto \omega^2/\mu \quad , \qquad (1)$$

where q is the spin-off rate, ω is the angular velocity, and μ is the precursor viscosity. Precursors with a viscosity of 10 cP gave poor surface coverage because the spin rate was such that too much precursor was removed, requiring a decreased spin rate from 3000 to 2000 rpm. Precursors with a viscosity of 20 cP were a good balance for the spin conditions of 3000 rpm and produced quality films with consistent thickness.

Cation concentration will also affect film thickness. Films produced from 5 layers of a 25% solution resulted in depositions as thick as 600 nm and a total thickness of approximately 3 μm, but the resulting films were filled with closed porosity and cracks parallel to the surface. All of the solvent and organic species were not able to pass through such a thick layer of material, and some were trapped. When the film was exposed to higher temperatures, the vaporization of these species caused the film to crack. Dense, crack-free films were produced consistently from 5% and 10% solutions. For a spin rate of 3000 rpm, a 5% solution with a viscosity of 20 cP produced films that were approximately 40 nm thick, while a 10% solution also having a viscosity of 20 cP produced 60 nm thick films. The viscosity of the 5% and 10% precursors were held constant by adding different amounts of methanol to each precursor; the volume of the 5% precursor was increased by 10% with methanol, the 10% precursor was increased by 20%.

The polymeric precursors were analyzed in a TG/DTA in air up to 800 °C at a rate of 10 °C/min (Fig. 2). The shapes of the curves were the same for all cation concentrations. The solvent is evaporated at low temperatures as indicated by the rising endothermic slope, re-
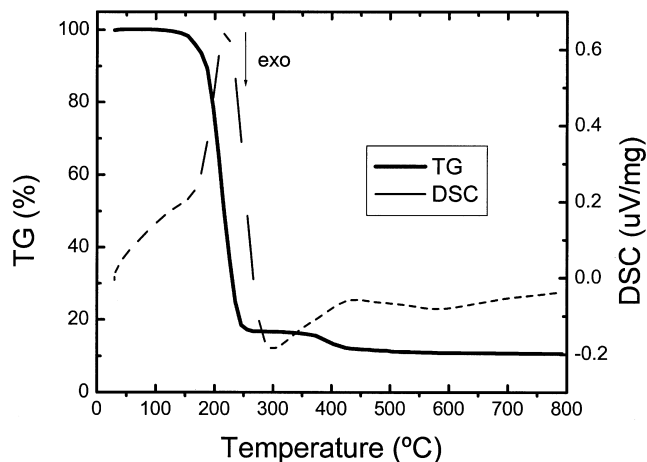
moving as much as 70% of the deposited material. At 165 °C, the slope changes as ethylene glycol begins to pyrolize, reducing the film to 20% of its starting weight. The decomposition of acetate groups is exothermic, occurring from 350 to 425 °C, removing an additional 5% of the weight. All organic species are removed by 425 °C, leaving nothing but YSZ as confirmed by XRD. Based on the density of the solvents used, this equates to the wet films being approximately twice as thick as the annealed film.

B. Microstructure

YSZ thin films were deposited onto single-crystal alumina and annealed at temperatures between 600 and 900 °C for 1 h. The grazing incidence XRD patterns (Fig. 3) indicate that the films are nanocrystalline, single-phase YSZ. Williamson–Hall plots were used to separate the effects of size and strain in the nanocrystals.[23,24] Grain growth in thin YSZ films is similar to the behavior that was observed for nanometer ZrO_2 particles.[25] A model of $D(T) = D_0 \exp[-E_a(T)/T]$ was used by Jouannen et al., where D is the particle size; $E_a(T)$ is the temperature dependent activation energy; T is the temperature; and $E_a(T)/T$ is shown in

$$\frac{E_a(T)}{T} = \frac{(E_{a1} + E_{a2})\left(\frac{1}{T} - \frac{1}{T_0}\right) - \left\{\left[(E_{a1} - E_{a2})\left(\frac{1}{T} - \frac{1}{T_0}\right)\right]^2 + 4\Delta^2\right\}^{1/2}}{2} \quad . \qquad (2)$$

In this relation, E_{a1} and E_{a2} are activation energies for the high- and low-temperature regimes, respectively; T_0 and Δ represent respectively the temperature and the width of the transition. By plotting the natural logarithm

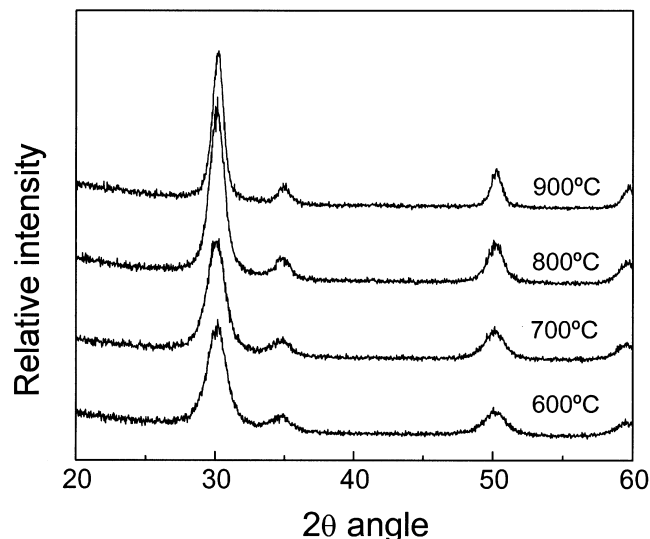FIG. 2. TG/DTA analysis of a 5% YSZ precursor.

FIG. 3. Grazing incidence XRD patterns of 150-nm-thick YSZ films on single crystal alumina, annealed at various temperatures.

of the grain size versus the inverse temperature, the activation energy can be determined (Fig. 4). The E_{a1} for the growth of nanocrystalline undoped zirconia powders was found to be approximately 0.34 eV ($T > 600$ °C).[23] The E_{a1} for nanocrystalline YSZ particles was calculated around 0.66 ± 0.01 eV. Thin film YSZ, however, possesses a lower E_{a1} (~0.45 ± 0.01 eV) than that of YSZ particles. Similar behavior has been observed in CeO_2 systems.[26] The difference in these two energies is primarily due to the constrained nature of the thin film.

Lattice strain was measured from the XRD patterns with Williamson–Hall technique. A sample annealed at 600 °C for 1 h on single-crystal alumina contains +0.31% strain. As the temperature is increased, this strain decreases, and reaches −0.11% at 900 °C (Fig. 5). Bulk YSZ and alumina have thermal expansion coefficients of 10.5×10^{-6} [27] and 8×10^{-6} K^{-1}, respectively.[28] If two bulk samples were joined, heated, and cooled, the YSZ would experience a tensile stress. Assuming that as the grains grow, the film will act more like a bulk sample, the film begins in a state compression on the substrate and develops tensile stress with grain growth. Further study is required to better understand this phenomenon.

Neither SEM (Fig. 6) nor AFM (Fig. 7) images of these films have shown any sign of porosity, either on the surface or in the bulk. All of the changes in the surfaces of the films can be attributed to grain growth. The optical density of YSZ films produced by a similar method was measured by ellipsometry and reported by Kosacki et al.[29] They found that at 400 °C, the films were approximately 90% dense and reached theoretical density by 800 °C. It is thus reasonable that the films investigated in this study experienced a similar trend.

SEM images of the surface also revealed defects ranging from 400 to 800 nm. The shape and structure of these defects suggest that they are the result of microscopic
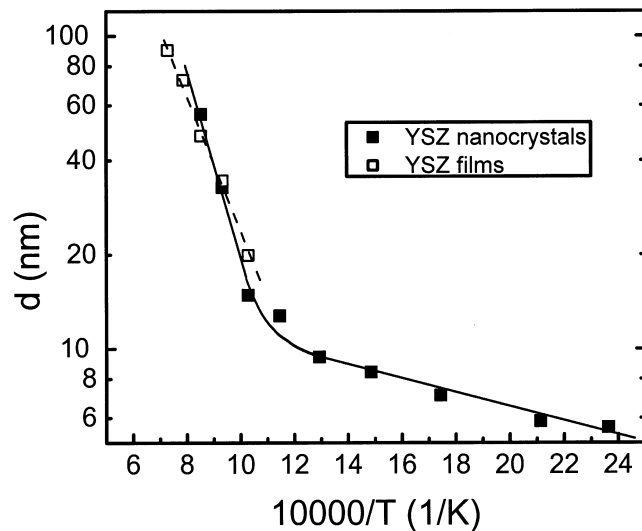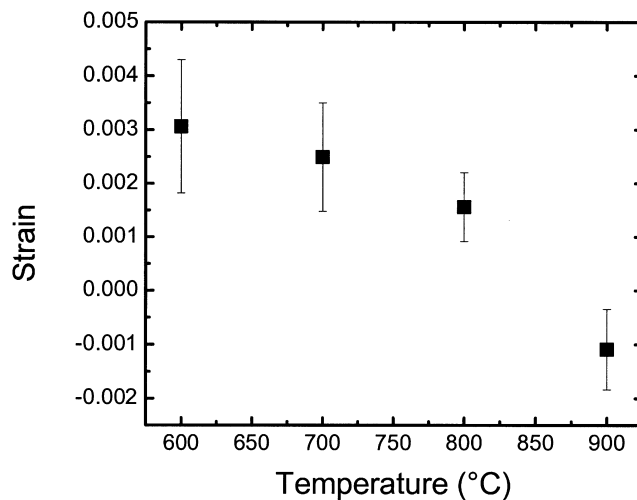

FIG. 5. Lattice strain of 150-nm YSZ films deposited on single-crystal alumina as measured from XRD results as a function of annealing temperature.
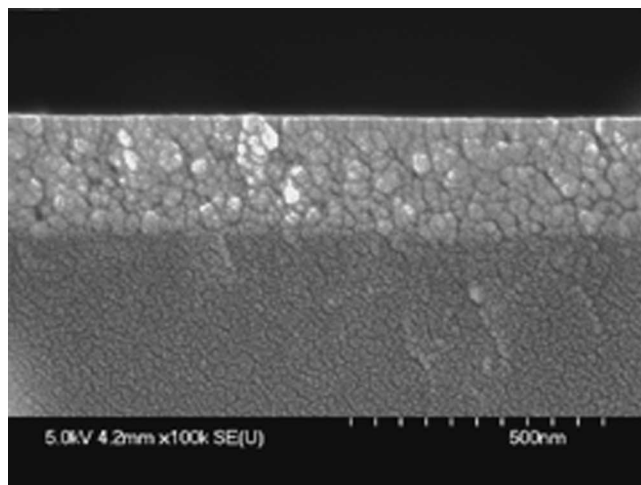

FIG. 6. Cross-sectional SEM image of YSZ on single crystal Al_2O_3.

FIG. 4. Plot of d versus $1/T$ for YSZ nanocrystals and thin films.

bubbles present in the precursor at the time of deposition. To prevent such defects from occurring, steps must be taken to remove all of the dissolved gas from the precursor, and then it must deposited in such a way as to prevent additional bubbles from developing in the solution.

IV. SUMMARY

A YSZ acetate-based polymeric precursor can be used to produce dense, crack-free thin films. The precursor can be fabricated under ambient conditions with only four constituents: zirconium acetate, yttrium acetate, ethylene glycol, and methanol. The precursor does not leave any extraneous dopants that could affect the densification or electrical properties of films. The precursor does suffer from aging when excess water is left in the system, increasing the viscosity of the precursor and ultimately
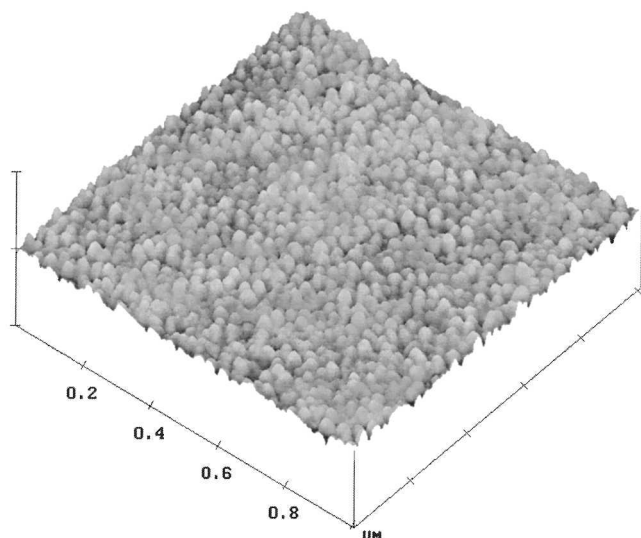
FIG. 7. AFM surface plot of YSZ film on Al_2O_3 annealed at 900 °C for 30 min.

forming a gel. This aging can be avoided by evaporating excess water and diluting the precursor with methanol.

Dense, polycrystalline films can be produced at temperatures as low as 600 °C. The activation energy for grain growth at $T > 600$ °C was approximately 0.45eV for thin YSZ films and 0.66 eV for YSZ particles.

ACKNOWLEDGMENT

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