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A Case Study in Striation Prevention by Targeted Formulation Adjustment: Aluminum Titanate Sol−Gel Coatings

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By careful consideration of the physical and chemical effects responsible for striation defect formation during spin coating, it is possible to adjust a coating solution's recipe to prevent these coating defects from forming. In this paper we present a specific "case study" to illustrate a useful reformulation strategy. Aluminum titanate (Al_2TiO_5) coatings were made via sol−gel chemical processing. An early version of our sol−gel recipe resulted in coatings that were severely striated and therefore unacceptable for their desired application, even though they had formed the correct crystalline phase during subsequent firing. The present paper examines that specific sol−gel recipe and illustrates a protocol for improving the final coating flatness by selecting a solvent additive that can influence the surface forces during drying. Coatings deposited with the modified solution were smooth and free from striations. The coating morphology was characterized by optical surface profilometry and crystallinity by X-ray diffraction. The widely applicable theory of targeted formulation adjustments to help eliminate striations during spin coating is discussed in light of the current experiments.

Introduction

Probably the most common and persistent defects that arise during spin coating are striations. These defects are radial ridges and thickness undulations that are aligned directly along the direction of flow imposed by the spin-coating geometry. This ridge structure does not occur near the center of the wafer where the radial outflow is slower. Instead a pattern results that is reminiscent of the shapes seen in buoyant Benard convection.[1]

Evaporation of solvent from the surface of the solution during spinning has been demonstrated to be the cause of these defects.[2,3] Daniels et al. noticed that "[w]hen evaporation was completely eliminated, by spinning the wafer in a totally closed, rotating chamber 10 mm × 100 mm, striations were eliminated completely" for their photoresist layers.[2] A similar observation was made more recently for sol−gel solutions.[3]

Daniels et al. also demonstrated that surface tension plays an important role in the formation of striations. They added unspecified "surface leveling agents" to their solutions,[2] which reduced the magnitude of the striations. The fact that the cellular pattern found at the wafer center is so similar in appearance to Benard cells is quite interesting too because surface tension was ultimately demonstrated to be the cause of the patterns that Benard observed a century ago.[4,5]

Recently, this background has helped provide a framework for understanding (and then preventing) the formation of striation defects as seen during spin coating.[6] This understanding and method are applied and illustrated in the present paper. The case study used to illustrate this technique is an aluminum titanate composition made via wet-chemical processing. Formulation modification was required because the recipe that was originally devised for this composition produced severely striated films.

Aluminum titanate (Al_2TiO_5) is attractive as a hard coat because of its near-zero thermal expansion coefficient and high melting temperature. These properties make it a good candidate for applications where thermal shock is a problem. As a coating, it may also be useful as a solid oxide lubricant or to provide a wear-resistant surface. Traditionally, aluminum titanate has been made by mechanical mixing and sintering of stoichiometric amounts of alumina and titania powders[7,8] and by chemical vapor deposition.[9] Mixed alumina and titania, whether from powders or gels, will form aluminum titanate above 1300 °C.[10] For the current study, we would like to deposit and form aluminum titanate

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on less refractory substrates, such as aerospace alloys, which will not withstand 1300 °C.

Others have made aluminum titanate via sol−gel processing, which is a wet-chemical route for preparing ceramic compositions. The sol−gel technique is attractive because it can provide high purity, compositional homogeneity, low-temperature processing, and ease of formation for monoliths and coatings.[11] The products of these studies were mostly powders or monoliths pressed from the sol−gel-derived powders. Depending on the synthesis, most investigators did not see the formation of aluminum titanate until at least 1300 °C,[12,13] similar to the more conventional synthesis routes. Although the sintering temperatures were similar to traditional powder processing, finer microstructures were produced that yielded better mechanical properties. On the other hand, there are a few reports of aluminum titanate formation around 800 °C with sol−gel processing.[10,14] Encouraged by these reported results, we wanted to deposit this composition onto low refractory substrates in the form of coatings. Thus, a precursor solution would need to be developed that would deposit uniform and stable aluminum titanate coatings at temperatures low enough to use on aerospace ceramics and alloys.

Initially, our sol−gel recipes produced coatings that were highly nonuniform and severely striated. In the present work, we describe and demonstrate a method for adapting some undesirable coating solutions to produce smooth, defect-free films. The following section is devoted to describing the physical and chemical processes involved in the growth and formation of striation defects. This illustrates how targeted solvent additions can help prevent striation defects from forming. After having discussed the theory behind targeted formulation adjustments, we will describe the synthesis of aluminum titanate precursor solutions and the deposition of coatings from these solutions. Characterization and results will center around two primary techniques: X-ray diffraction (XRD) and surface profilometry. The former will show that we are forming the desired phase (i.e., Al_2TiO_5), and the latter will reveal surface morphology of the layers (and how it depends on the solvent mixture used in the sol−gel recipe). We will then discuss the results and relate them to our striation-prevention model.

Background

As noted in the Introduction, striation defects are driven by solvent evaporation under conditions that naturally impose composition gradients in the near-surface region of the coating solution. As a result, the surface tension at the top surface will be changing during the spinning process. The near-surface region can then be susceptible to lateral capillary instabilities, known as “the Marangoni effect”.[15] By analogy to the thermocapillary convection process, it has been conjectured that this capillary instability found during spin coating arises when the surface tension *rises* during solvent evaporation. Thus, the coating reformulation strategy is based on adding solvents so that the surface tension will be *reduced* during the naturally occurring evaporation that is found during spin coating. This requires careful assessment of surface tension and vapor pressure values attributable to the various solvents that make up the coating solution.

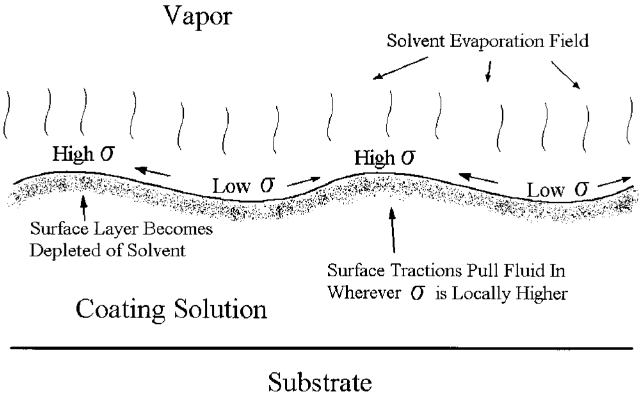

Figure 1. Schematic illustration of the capillary instability that operates during the drying stage of spin coating. Evaporation can result in a solvent-depleted surface layer having a different surface tension than the underlying solution. This condition can be unstable when the surface layer has a higher surface tension. Note that areas labeled “high σ” and “low σ” both have higher surface tension values than that of the starting solution but represent random variations in composition that then lead to lateral fluid motions, building the striation structures.

Figure 1 illustrates how the capillary instability can arise as a result of solvent evaporation.[6] The solvent evaporation field is initially uniform everywhere—largely controlled during spin coating by the vapor boundary layer through which all evaporating species must diffuse to reach the unsaturated ambient. When the surface layer composition starts to deviate significantly from the starting composition, capillary effects become important. If the surface layer has a composition that results in a *higher* surface tension, then an instability can arise. The instability operates by the amplification of tiny, naturally occurring, random, compositional differences at the surface (causing local surface tension differences). Any local difference in surface tension causes lateral traction and fluid motion: areas with slightly higher surface tension pull together, while areas with slightly lower surface tension are stretched out. The capillary-driven lateral motions of fluid at the surface are the Marangoni effect,[15] and both thermal and compositional variations in surface tension can cause such lateral motions. This process is unstable whenever the growth of random bumps amplifies and enhances the surface tension difference that caused the motions in the first place.

Under the present processing conditions, the Marangoni effect becomes unstable if two related effects occur simultaneously. First, the evaporation process at high and low spots must occur at slightly different rates. Typically, the diffusion of the solvent from lower strata

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of solution to accommodate the evaporation process will be slower in thicker locations, causing the composition at the tops of slight humps to be more strongly depleted of solvent. Second, the compositional dependence of the surface tension must be aligned so that, as these composition differences develop, the high spots must evolve surface tension values that are larger than those found at the troughs. If these two conditions are met, the spin-driven evaporation can become unstable and striation defects can form.[6] Thus, the coatings that we examine after spin-on are the result of several competing and simultaneously acting kinetic effects.

Recently, a strategy has been proposed to prevent or drastically reduce the instability described above during spin coating.[6] Because the main driver of the instability is compositional changes at the surface that raise the surface tension, the striation prevention strategy is based on reformulating the coating solution so that surface tension actively drops during the critical stages of spin-on. Thus, the two key factors to consider when choosing solvent additions are their vapor pressure and their surface tension values. Because the evaporation process preferentially removes the most volatile components, additives must be chosen that whatever is left behind and enriched at the surface will cause the surface tension to decrease. These are not surfactants, per se, but instead act as cosolvents that are sequentially removed during drying, thereby exerting control over the local surface tension to prevent this particular Marangoni instability.

Experimental Procedure

Aluminum tri-*sec*-butoxide (ATSB) was weighed and put into a round-bottomed flask with a stir bar in a drybox. The flask was sealed with a rubber septum and removed from the drybox. Distilled isopropyl alcohol (IPA) was added by syringe under nitrogen and stirred (15:1 = IPA:ATSB). After 1 h, ethyl acetoacetate (EtAcAc) was added by syringe and the solution was stirred (1:1 = EtAcAc:ATSB). In a separate flask, water was diluted in IPA to produce a 4:1 molar ratio of water to ATSB and a final IPA concentration of 20:1. After an additional 3 h, the water/IPA mixture was added slowly to the solution. Titanium(IV) isopropoxide (TIP) was then added dropwise to the solution under nitrogen to yield a 1:2 molar concentration with the ATSB. The final solution was allowed to stir overnight. The solution turned cloudy after the TIP addition and cleared over several days or immediately with refluxing.

The coating solution was filtered with a 0.2 μm syringe filter before coating. Several drops of solution were deposited onto cleaned silicon and spin coated at 2500 rpm. Ambient conditions in the coating chamber were 24 °C and 10% relative humidity. The samples were first dried at 100 °C for 15 min and then placed into a hot furnace at 400 °C for 1 h. A corner of each coating was scraped off the substrate with a clean razor blade before the final firing step.

Powders were made from the same precursor solutions by allowing them to dry in a watch glass under ambient conditions. They were dried further at 100 °C for several hours and then at 250 °C for several more hours. The powders were fired in alumina crucibles at various temperatures as reported with the data. These powders were analyzed by XRD.

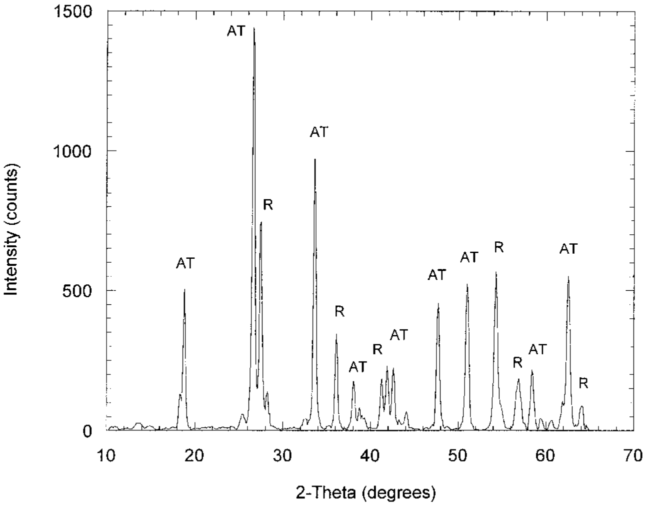

Figure 2. XRD pattern of powder obtained after drying and firing of the precursor solution to 850 °C. AT = aluminum titanate, and R = rutile.

The recipe described above produced coatings with high roughness as a result of striation defect formation. Targeted solvent addition was made based on the solution's major solvent constituent: IPA. In this case, we chose a single additive that was more volatile (9.7 kPa vapor pressure versus 5.3 kPa) and had a higher surface tension (23.9 mN/m versus 21.7 mN/m) than IPA. A solvent that met these criteria and was simple enough and unlikely to disturb the sol−gel chemistry was ethyl acetate (EtOAc). Other important factors in our opinion related to probable miscibility with the existing solution and relative safety. The modified solution was subsequently made by mixing 10 mL of the original coating solution with 5 mL of EtOAc in a separate round-bottomed flask. A significant quantity of this second solvent was required to ensure that the overall solution had a surface tension that would change appreciably during solvent removal during spinning. This solution mixture was stirred for a few minutes before coating. The appearance of the modified solution before coating was similar to that of the original solution. Films were deposited from the EtOAc-modified solution similarly to the unmodified coatings.

The microstructure of the aluminum titanate composition at various temperatures was characterized by XRD (Seimens D-500). Spectra were taken using Cu Kα radiation between 10° and 70° 2θ at 0.05° increments. The morphology and thickness of the deposited films were examined with optical surface profilometry (Wyko RST Plus). Through optical interferometry using white light, the RST Plus renders a three-dimensional representation of a surface with roughly 5 Å resolution in the *z* direction. When an edge of the coating was scraped before firing, a discrete step was formed to measure the thickness of the film.

Results

After pyrolysis to 850 °C, the pseudo-brookite Al_2TiO_5 phase was formed from the Al_2O_3/TiO_2 precursor solution. As a minor phase, rutile was also present. Figure 2 shows an XRD spectrum of the powder that was obtained from a dried and fired precursor solution. As can be seen by the absence of alumina peaks in Figure 2, all of the alumina from the precursor has been converted to aluminum titanate. Even after the powders were fired to 1350 °C, rutile was still present with the aluminum titanate from both the unmodified and EtOAc-modified precursor solutions (Figure 3).

Coatings made with the original solution were severely striated. The striations were 300 nm high, with the trough between the striations being apparently flush with the substrate (i.e., there were probably discontinuities and dewetting between the striation ridges in these films). This case is shown in Figure 4. The roughness (Ra) of these coatings was 75 nm. With EtOAc modification, surface roughness was reduced to 1.4 nm (Figure 5), which is near the lower limit of the optics in our instrument.

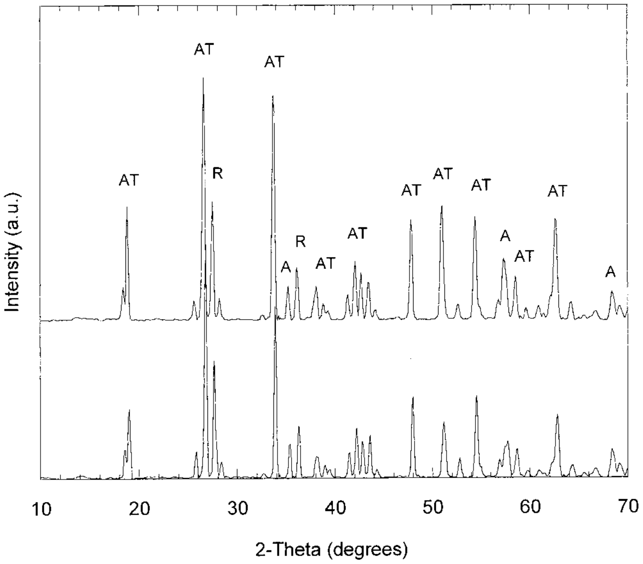

Figure 3. XRD patterns of the powders from the original (bottom) and EtOAc-modified (top) sol−gel solutions after drying and firing to 1350 °C. AT = aluminum titanate, R = rutile, and A = alumina (corundum).

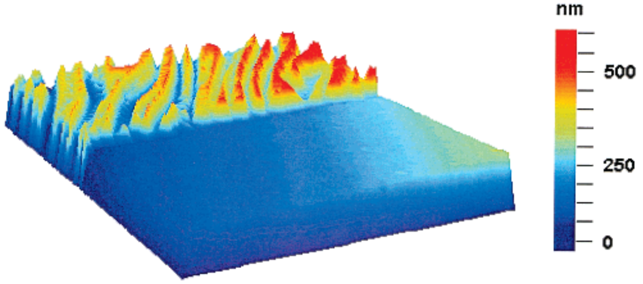

Figure 4. Surface topography of the texture and structure found after coating with the initial coating solution—before modification with EtOAc. The micrograph is looking at the side of the coating from an area where the coating was scraped away to illustrate the magnitude of the striations.

Discussion

In the Experimental Section, we described a recipe for producing high-quality films of aluminum titanate at moderate temperatures. To take advantage of the lower processing temperatures offered by sol−gel processing, we had to optimize the chemistry to form the proper network in the gel *before* firing. The current method began by prehydrolyzing the aluminum precursor and subsequently adding the faster reacting titanium precursor in the presence of a reaction inhibitor. In this way, mixed metal oxide bonds are thought to have formed (e.g., Al−O−Ti), which promoted Al_2TiO_5 formation over the constituents' respective phases—alumina and rutile. The reports mentioned earlier that did not produce Al_2TiO_5 below 1300 °C most likely did not form mixed metal oxide bonds in solution before firing.

With the chemical solution method described here, aluminum titanate started to form around 750 °C and had fully consumed the available alumina by 850 °C—several hundreds of degrees lower than that by melt processing. The XRD spectra remained similar at 1350 °C and retained a minor phase of rutile. The similarity of the spectra showed the ability to produce aluminum titanate at 850 °C that had the same microstructure as it did at 1350 °C. Although the tribological properties of the Al_2TiO_5/TiO_2 coatings were not tested in this work, previous investigations have shown that enhanced friction and wear properties resulted from nickel titanate coatings that contained substantial amounts of rutile.[16] Because the goal of this paper was to deposit defect-free films of this composition, we concentrated on targeted formulation adjustments to achieve defect-free films rather than on obtaining single-phase aluminum titanate coatings.

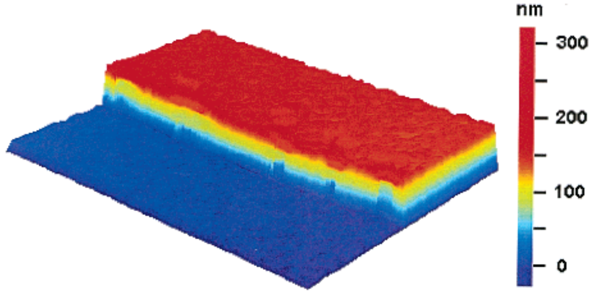

Figure 5. Surface topography illustrating a smooth coating after the addition of EtOAc to the original sol−gel solution. The view presented here is an edge of the coating formed by scraping away a portion of the coating. The surface roughness for this sample was reduced more than 50 times compared to the sample shown in Figure 4.

After the XRD results showed the desired phase, it seemed possible to make aluminum titanate coatings at temperature low enough to use aerospace alloys for substrates. However, when films were deposited from these precursor solutions, it was obvious from examining the morphology of these coatings that they would not be practical for any tribological or corrosion-resistant applications. It was at this point that we employed the concepts and theories of defect formation in spin-coated films. We examined the evaporation of the solvent system and decided to add a cosolvent instead of starting with a new chemistry.

In the present case, a single solvent added to a stable sol−gel coating solution has resulted in better than a factor of 50 improvement in coating flatness. This is interesting because the original volatile constituents were retained and would also have necessarily been removed during the spinning and subsequent drying. Thus, the EtOAc addition was successful at managing the evolution of capillary forces during spinning—at least for times when the coating was still fluid enough that unstable flow *might* have been instigated. In this case, the capillary instability was prevented by careful solution reformulation.

This technique should be widely applicable to sol−gel and other types of spin-on solutions that happen to develop striation defects. Careful management of the evaporation sequence and drying during spinning must be done to ensure that the surface tension at the free surface is lower than that of the parent solution—at least during times when the coating still contains enough solvent to be reasonably fluid. Future studies are planned to model the kinetics of this dual solvent coating and drying process for spin-coating deposition. More in-depth modeling might allow us to understand

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the amount of secondary solvent required and the importance of viscosity in controlling the roughening even when capillary forces are unfavorably aligned.

Conclusions

By the method described in this paper, we demonstrated the ability to produce aluminum titanate at temperatures much lower than those required by melt processing. As shown by XRD, Al_2TiO_5 was the only Al-containing phase formed when the precursors were fired to 850 °C. Rutile was also present as a minor phase at this moderate temperature, as well as at 1350 °C. Coatings deposited from the initial unmodified precursor solution were severely striated. Using careful solution reformulation, smooth, defect-free films were made by the addition of EtOAc to the precursor solution before spin coating. Thus, sol–gel techniques proved to be adequate for producing the desired composition, while solvent adjustment was important for obtaining flat coatings of the correct phase.

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