Chapter 5

Discussion

The research of this thesis has been designed to explore the relationship between process conditions in a plasma-assisted directed vapor deposition system and the atomic structure of synthesized metal oxide thin films. Indeed it has generated information about the effect of plasma activation, substrate biasing and substrate temperature on the DVD thin film deposition of ceramic materials. This discussion chapter will consider the observed film structure trends, discuss the various physical phenomenon motivating observed trends, and give suggestions for future, related work with the DVD system. This chapter will also address the particular question of DVD suitability for synthesis of solid oxide fuel cell electrolyte membranes.

5.1 Density of metal oxide deposits

As noted in Chapters 1 and 2, the ability of plasma-assisted DVD to create dense layers of metal oxide has not been systematically examined and reported prior to the work of this thesis. The material synthesis conditions selected and the material characterization techniques employed for sample analysis in this research were thought to offer
opportunities for discovery and confirmation of dense metal oxide fabrication. Indeed, the deionized water test results of Chapter 4 reveal a trend in which denser films are created by the systematic application of additional plasma-assisted DVD process technologies. Specifically, deionized water testing shows that the water does not absorb into the deposited film and anode substrate of samples 6, 7, and 8. These results suggest dense film creation.

Closer inspection of these results suggests that the underlying cause of the positive water tests on samples 7 and 8 is unclear, with the result being generated by either dense film deposition or anode polishing. Separate deionized water droplet testing on a polished anode substrate surface prior to YSZ deposition revealed that a water droplet would remain intact on the polished surface, in contrast to the rapid absorption of a droplet on an as-received substrate surface. Thus, it appears that the positive results for these two samples could be caused by substrate polishing and/or dense film deposition. The SEM images of sample 8 (Figs. 4.46 - 4.50) show a very thin film with distinct porosity between deposited oxide regions. For this sample, it appears that the positive water droplet result has most likely been generated by polishing of the anode surface rather than deposition of dense YSZ. The positive deionized water test for sample 7 could be the result of substrate polishing, as suggested by the result for sample 8, and dense deposition, as suggested by the result for sample 6.

The positive deionized water test result of sample 6 appears to provide the strongest evidence that DVD has the ability to create dense metal oxide layers. Specifically the application of DVD plasma activation (120 A) and substrate biasing (200 V AC bias with 24 μsec positive and negative pulses), the experimental conditions of Table 3.1, and the system geometry configuration of Fig. 3.1 appear to create a film that resists the
absorption of deionized water. While samples 6 and 7 are dense enough to prevent rapid penetration of water through the film, the micrographs of Figs. 4.34 - 4.38 and Figs. 4.40 - 4.44 do not reveal the fully densified film envisioned at the outset of the project (e.g. Fig. 2.4c for alumina films). Instead, the micrographs reveal dense, columnar structures that are more like those found in Fig. 2.4b. The structures of samples 6 and 7 appear to be those described by Thornton as Zone T or Zone II microstructures [64], typified by dense columns of material with little open porosity from top to bottom in the structure, Fig. 5.1. (The film shown in Fig. 2.4c is more likely a Zone III structure.) While Thornton correlates changes in film density to changes in substrate temperature or background chamber pressure, recent research analysis suggests that atomic structure changes from Zone I to Zone III occur more generally because of an increase in the

Figure 5.1 Thornton’s zone diagram. Experimental study of sputtering (e.g. Ti, Cr, Fe, Cu, Mo, and Al) has revealed repeatable microstructural trends [64].
energy available to atoms arriving at the film growth surface, either as the result of 
substrate heating or the actual deposition process [16, 70]. Since the process conditions 
used with samples 6 and 7 have generated deposits denser than the other six experiments 
it is useful to examine these process conditions in more detail and suggest reasons why 
they have proven best for dense metal oxide film creation in the plasma-assisted DVD 
environment.

In the experiments that produced samples 6 and 7, the 120 A current of the hollow 
cathode plasma unit and the 200 V potential of the substrate bias were unchanged from 
the conditions used to fabricate sample 5, a sample that partially resisted deionized water 
penetration. In contrast to the experiment for sample 5 which employed a DC substrate 
bias, the experiments for samples 6 and 7 utilized an AC 200 V potential with 24 µsec 
dwell time of both the positive and negative potential. Apparently the shift from DC to 
AC bias enhanced the ability of the neutral adatoms and depositing ions to organize into a 
dense structure. While a detailed understanding of the link between AC bias conditions 
and film densification is beyond the scope of this thesis, it does seem possible to propose 
some initial qualitative explanations for the observed trend.

As noted in Chapter 4, samples 4 and 5 partially resisted deionized water penetration 
through their coatings. These results suggest that plasma activation (120 A) and DC 
substrate bias (50 or 200 V DC−) stimulated some film densification. This trend matches 
the results reported by Tsai and Barnett [49] and Morgner [56], although in both literature 
reports the densification appears to have been more complete than the DVD results of this 
thesis. Interestingly, the results for samples 6 and 7 suggest that application of an AC 
substrate bias is more effective than a DC bias for film densification.
It is reasonable to assume that the use of an AC bias rather than DC leads to attraction of different atomic and molecular species to the surface of the growing film during the negative and positive portions of the bias cycle. Under all bias conditions, neutral metal and gas species will contact the growth surface. In the DVD process, these neutral species are expected to constitute the majority of all atoms and molecules being deposited, on the order of 70% or more of the depositing species [56]. Within an argon plasma such as that generated by the DVD hollow cathode system, positively charged argon atoms and metal atoms (e.g. Y and Zr) are expected to be present to bombard or deposit onto the coating surface during the negative portion of the bias cycle [71]. Survey of the literature also suggests that some of the oxygen atoms and molecules from the YSZ source rod and the carrier gas flow will be positively charged and thus attracted to the coating surface during negative pulses [72]. During the positive portion of the AC pulse, negatively charged oxygen ions and free electrons are expected to be available for deposition on and interaction with the growing film surface [72]. Introduction of negative oxygen ions and free electrons into the surface coating process, combined with positive species deposition during just half of the process has led to a somewhat denser coating. The density increase could result from one or more of the following factors.

First, in separate DVD experiments, application of a positive bias to a coating surface has been noted to generate a significant rise in the temperature of the coating surface, in some cases melting high temperature molybdenum substrates [73]. Attraction of electrons to the coating surface in the experiments here could have had a similar effect, raising the deposit temperature closer to its melting point. As shown in the Thornton diagram of Fig. 5.1, higher substrate temperatures lead to denser coatings.
Second, introduction of additional oxygen into the deposition process, during the positive portion of the bias cycle, could lead to creation of a film that is more stoichiometrically-correct, more regular, and thus denser. During the various deposition experiments performed for this thesis and other related experiments [74], subtle color changes have been observed in deposited YSZ films. Films deposited without a substrate bias were often slightly gray unless higher oxygen flow rates were employed. Those films deposited with a bias were whiter or, in the case of AC bias, more transparent, suggesting a preferred stoichiometry and increasingly dense coating. In other work, this color change has been attributed to changes in the oxygen content of the film [61]. Subtle changes in the stoichiometry of the films from sample to sample should be evident in the XRD scan results of Chapter 4. Indeed careful inspection of the peak positions in the different scans does reveal slight variations in location that could be the result of small changes in film composition.

Third, inspection of Figs. 4.31, 4.37, and 4.43 suggests that the films of samples 6 and 7 are slightly thinner than the film of sample 5, 13 \( \mu \)m thick versus 15 \( \mu \)m. A thinner coating would correspond to a reduced deposition rate that allows adatoms more time to organize on the coating surface prior to being buried in place by newly depositing material. Though unlikely to be the sole cause of film densification, slower deposition rates are known to enhance deposit density [16].

Before leaving the discussion of metal oxide film density as generated by plasma-assisted DVD, it seems important to consider why the dense films of this study are not as dense as those reported in the literature ([49], [56], and Fig. 2.4). Although a definitive statement is not possible, it seems reasonable to suggest that some fraction of the density difference is due to a difference in the energy of the neutral species in the DVD system when
compared with the sputtering and electron beam evaporation experiments of [49] and [56]. Sputtering systems are known to generate neutral particles with an average kinetic energy of 5 eV and a high energy distribution ranging up to several tens of eV [75]. Standard electron beam evaporation systems are known to generate neutral particles with an average kinetic energy of 0.2 – 0.6 eV [16, 76]. Previous model-based study of neutral species in the DVD environment has revealed that such neutrals have on average just 0.05 eV of kinetic energy [16]. In the DVD system the lower kinetic energy is the result of vapor atom collisions with background gas atoms that are moving at slower velocities. These collisions lead to thermalization of the vapor atoms. It appears that the silica deposition results reported by Morgner et al. [56] and noted in the Literature Review are the result of a similar thermalization effect. As summarized Chapter 2, while their plasma-assisted deposition experiments at 0.4 Pa chamber pressure generated dense coatings, similar activated electron beam deposition at higher chamber pressures (e.g. 0.7 – 1.7 Pa) generated columnar structures [56]. The pressure in the DVD chamber during deposition was 8 Pa, perhaps explaining the dense but columnar structures observed here.

5.2 Deposition rate

One of the interesting and somewhat unexpected trends revealed by the experiments of this thesis was the dramatic decrease in deposition rate or deposition efficiency caused by application of the different DVD process controls (i.e. plasma activation and substrate biasing). The dramatic decrease in deposited film thickness is apparent in Fig. 4.55, and the trend is summarized below in Fig. 5.2.

The link between plasma activation and reduced YSZ deposition rate as observed from experiments 1 to 2, 3 to 4, and 7 to 8 appears to be fairly understandable. As shown in
Fig. 2.3b, Fig. 3.14, and in more detail in Fig. 5.3, the flow of plasma electrons and ions

Figure 5.2 **Effect of DVD process controls upon deposition rate.** Application of plasma activation and substrate biasing led to significant reductions in YSZ deposition during each 20 minute experiment.

Figure 5.3 **Intersection of plasma and carrier gas flows.** The perpendicular intersection of carrier flow and high energy plasma flow disrupts the directed momentum of the vapor towards the coating surface.
out of the DVD hollow cathode unit is perpendicular to the carrier gas and YSZ flow emanating from the vapor source and directed towards the coating surface. The intersection of perpendicular gas and vapor flows has been shown to redirect such flows significantly, modifying the directed momentum of vapor streams and affecting deposition efficiencies onto surfaces [16, 52]. It should be noted that in references [16] and [52], the intersecting flows are both composed of neutral gas and vapor atoms. In the current experiments, the hollow cathode flow also includes ionized argon atoms and free electrons.

Interestingly, as the electron current of the low voltage electron beam (LVEB) in the plasma flow increases, there appears to be a resulting drop in YSZ deposition efficiency on the anode surface. While a full explanation of the link between LVEB current and deposition efficiency is beyond the scope of this thesis, it can be noted that Morgner et al. state that ionization of gas and vapor atoms in a hollow cathode plasma leads to an increase in the kinetic energy of ions in the system, even without application of an electrical bias on the coating surface [56]. Once these ions reach higher kinetic energy levels, it is not at all certain that their enhanced momentum will be directed towards the coating surface. Thus, as the plasma current increases from 60 to 120 and then 180 A, more ions are created in the system with elevated kinetic energies. If this energy is not directed towards the coating surface (and there is no reason to believe it will be), the result could be decreased deposition rates as ionized and neutral gas and vapor atoms are scattered from the initially directed carrier gas / vapor atom flow emanating from the DVD nozzle (Fig. 3.14).

The other interesting relationship shown in Fig. 5.2 is that between deposition rate and substrate bias. In Fig. 5.2, the largest drop in deposition efficiency and rate occurred
when a 50 V DC+ bias was applied to the coating surface. A smaller but equally distinct drop in deposition efficiency was observed when the DC+ substrate bias was increased from 50 to 200 V. The exact cause of this relationship is unclear. It could be the result of ion bombardment and resputtering as observed by Tsai and Barnett [49]. Without additional investigations, the exact cause of the link between deposition rate and substrate bias will remain uncertain.

Observation of the dramatic drop in deposition rate (Fig. 5.2) might suggest that DVD cannot produce dense electrolyte membrane layers at “high” rate. For experiment 6, the deposition rate is approximately 0.75 µm/min (40-45 µm/hr). While this rate is obviously lower than the 1-15 µm/min envisioned at the outset of this thesis and lower than what DVD can achieve for porous metal oxide coatings (experiment 1), it is actually quite high when compared with the rates of other techniques being examined for the creation of solid oxide fuel cell electrolyte membranes. A chart of deposition methods compiled by Will et al. [42] shows that, of the other deposition methods available for dense coating fabrication, only spray pyrolysis and electrochemical vapor deposition (EVD) can match the DVD dense-film deposition rates recorded here. It should also be noted that EVD requires the use of corrosive gases, and spray pyrolysis coatings often must undergo a post-deposition heat treatment to ensure pinhole-free coatings. So, even though the DVD coatings are not as dense as desired and even though the deposition rates are not as high as desired, the plasma-assisted DVD coating method does show promise as a method of creating dense, pinhole-free electrolyte membrane layers for solid oxide fuel cells.
5.3 Future Work

The experimental study of this thesis has revealed distinct trends in metal oxide deposition density and deposition rate in the plasma assisted DVD environment. The work has shown that plasma activation and substrate biasing can be used in a DVD environment to increase the density of depositing metal oxide films. Still, the underlying cause of film densification has not been definitively identified in this thesis, and there is clearly room for further film densification as the deposited coatings of this thesis are Zone T or Zone II structures, not fully dense, recrystallized Zone III structures.

To determine whether the denser coatings of samples 6 and 7 are the result of the combination of the three factors suggested here (and others) or the result of just one factor will involve additional detailed experimental work as a follow-on to this thesis. As noted in Chapter 3, measurement of substrate temperature during application of the AC pulse bias is complicated since the metal wires of a standard thermocouple act as a short-circuit that prevents charging of the substrate surface. To investigate the electron heating question, measurement of substrate temperature during AC biasing of the substrate will need to involve some type of non-contact (e.g. pyrometer-based) sensor. Information about the specific stoichiometry of the deposited films could be obtained via a host of quantitative chemical analysis techniques that are more sensitive than the XRD technique employed here. Such techniques could include SEM-based energy-dispersive x-ray spectroscopy, transmission electron microscopy, particle-induced x-ray emission, and x-ray fluorescence techniques [77]. Finally, a more accurate determination of material deposition rates might simply involve doubling of the deposition time from 20 to 40 minutes, creating a more definitive difference in deposit thickness.

Efforts to increase the density of films deposited in a plasma-assisted DVD environment
could involve additional explorations. Hass et al. have suggested that modification of the DVD gas flow nozzle could allow the process chamber pressure to be lowered while still allowing vapor to be focused and directed to the coating surface [78]. Further experimental and model-based investigation of such modifications appears warranted given the pressure dependence of coating density observed in this study [16, 56, 79]. Direct simulation Monte Carlo models appear to hold promise as a means for better understanding of the plasma, vapor, and carrier gas interactions experienced in plasma-assisted DVD [80, 81].

Additionally, Morgner et al. [56] suggest that film densification should be possible using only plasma activation without substrate biasing. To explore their assertion more fully, a new set of DVD experiments could be performed in which hollow cathode plasma current is raised from 60 to 120 to 180 A without application of any substrate bias. Such experiments should eliminate the loss of deposition rate caused by application of a substrate bias while also creating dense Zone II or Zone III coatings.

Further examination of AC pulse bias parameters also appears prudent. In this thesis, the selection of pulse length (24 µsec +/-) was somewhat arbitrary. The results of experiments 6 and 7 suggest that this AC bias setpoint generated a denser coating. However, there is no reason to believe that the 24 µsec pulses are optimized. The DVD system allows the positive and negative pulse lengths to be set independently over a broad range (4 – 815 µsec). Thus, there could be a setting which maximizes film densification while also maximizing deposition rate [50]. The subtle effects of the AC pulse bias upon DVD film synthesis remain largely unexplored.

Finally, since the original motivation of this thesis work was creation of electrolyte membrane layers for solid oxide fuel cells, it seems appropriate to suggest that dense
DVD-synthesized electrolyte membrane layers should be incorporated into fuel cell assemblies to judge the power production capabilities of these materials.