Chapter 12

Discussion

As noted at the outset of the Introduction chapter, this dissertation has recorded the invention and initial experimental and theoretical investigation of a new physical vapor deposition technology - Directed Vapor Deposition. Prior to the commencement of this project in 1992, the concepts behind Directed Vapor Deposition technology were untested and in many cases not yet clearly defined. The work of this dissertation has refined and developed those initial ideas and reduced them to practice as a functioning materials synthesis system. The preceding chapters not only describe the synthesis tool design pathway from concept to functioning system but also they present a significant volume of experimental and theoretical information which allows an initial assessment of DVD's utility to be made. In Chapter 3, a long list of possible material processing features of DVD was presented. In light of the work presented in this dissertation those suggested advantages of DVD can now be reviewed and the ability of the technology to deliver those advantages can be assessed.

12.1 Focus, Efficiency, and Angular Distribution

The first point of Chapter 3 stated that DVD should be able to entrain and focus vapor atoms in a carrier gas stream for efficient deposition at selectable angles. Under certain conditions, the technology has demonstrated its ability to deliver some of this advantage. As clearly demonstrated in Fig. 5.12 b) the technology is capable of focussed deposition on substrates like fibers, and Fig. 7.8 shows that deposition on such substrates is more efficient than conventional high vacuum e-beam processing. These results certainly suggest that DVD could make a contribution to industrial coating of continuous fibers for metal matrix composite applications.

When coating flat substrates, it is not quite so clear that DVD is a superior processing pathway. Fig. 10.13, which compares model predictions of DVD film thickness profiles with conventional e-beam vapor deposition profiles, indicates that DVD can increase vapor deposition focus. However, Figs. 5.12 a) and 7.2 illustrate that, while focussed, the efficiency of this deposition is far less than desired. Indeed much of the vapor which reaches the vicinity of the substrate is carried away from possible deposition by the wall jet (c.f. Fig. 10.3), leading to deposition efficiencies below the level of conventional e-beam systems. The vapor transport model for DVD does provide insight into how the deposition efficiency of this technology could be improved to exceed that of conventional techniques through reconfiguration of the system.

The model also suggests that DVD does not afford materials engineers with the ability to vary deposition angle or angular distributions (Table 10.1 and Fig. 10.11). In all cases examined, the angular distributions are broad, with an average deposition angle greater than 30^{o} from the normal. As noted in the dissertation Introduction, it was thought that if DVD could deposit material at angles less than 10^{o} from the normal, it might prove useful for microelectronic via filling. Although via filling has not been specifically examined either experimentally or theoretically, the work of this dissertation allows an assessment of the technology's applicability to be made. Specifically, study of Fig. 10.5 does not reveal any conditions under which the average vapor atom angle is even close to 10^o in the vicinity of the substrate. Thus it does not appear that DVD technology is well-suited for the microelectronics via filling application.

12.2 Non-line-of-sight Coating

The second point raised in Chapter 3 suggested that DVD could have an ability to deposit vapor onto substrate surfaces not in the line-of-sight of the vapor source. Fig. 7.9 clearly shows that DVD has this ability. The desire to coat metal matrix composite continuous fiber reinforcement quickly and efficiently represented the primary motivating application for Directed Vapor Deposition development. At the inception of the project it was hoped that DVD would be able to surpass the capabilities of conventional sputtering or e-beam systems and offer a viable high rate, high efficiency material synthesis alternative. The experimental results of Chapter 7 show that DVD can more than double vapor deposition efficiency onto fiber reinforcement while rapidly coating fibers from a focussed vapor stream.

SEM study of the metal coated fibers reveals that the cause of the increased efficiency is vapor deposition on portions of the fiber surface not in the line of sight of the primary vapor flux. Recent use of DSMC simulation programs produced by Bird [235] confirms the suggestions of Hill [79] that the non line-of-sight coating is the result of vapor atom collisions with gas atoms, collisions which redirect vapor atoms into contact with the top, bottom, and back side of the fiber. This ability of DVD to more than double line-of-sight deposition efficiencies through use of its focussed gas jet should appeal strongly to companies interested in decreasing fiber coating costs.

One major concern regarding DVD deposition onto fibers has to be the low energy of deposition which creates porous, columnar microstructures (Figs. 2.8 and 7.9). McCullough et al. [20] have demonstrated that such structures allow significant oxygen incorporation into deposited films, leading to the formation of unacceptably brittle microstructures. Some additional means of producing a dense microstructure via DVD could be required before the method can be seriously considered for this application (e.g. Dugdale's heating of the chamber gas [50, 84] or activation of the vapor stream as demonstrated by various individuals at F.E.P. [240-243])

For industrial coaters of fiber, the visualization work of Chapter 5 and the modeling work of Chapters 10 and 11 indicate that the current DVD system configuration may be the preferred setup for the fiber coating application. Figs. 5.12 and 10.2 show that using the gas jet to bend the vapor stream 90^{o} towards the substrate not only creates an environment in which non-line-of-sight coating can occur but also it leads to much more significant vapor focusing than is evident in the simulations of the reconfigured system (Fig. 11.4). The original DVD system design presents a narrow region through which rotated fibers can be horizontally passed for uniform, high rate (50 - 100 μm/min.), high efficiency vapor deposition. These results suggest that it may be possible to accomplish industrially acceptable high rate fiber coating using a fairly small, low-cost e-beam gun system, perhaps even a system the size of the experimental setup developed for this project.

12.3 Vapor Stream Mixing

The third point of Chapter 3 suggested that DVD's use of a gas jet could facilitate mixing of vapor atoms from adjacent sources. This concept was not experimentally explored in this dissertation and the limitations of the model preclude theoretical examination of the issue. To assess more fully the ability of DVD to coat fibers in an industrial setting, research should be conducted which will demonstrate the technology's ability to deposit the correct alloy compositions desired for the metal matrix composite fiber application (e.g., Ti-6wt%Al-4wt%V) [20]. Single crucible evaporation of this alloy system using DVD will almost certainly experience the same stoichiometry problems observed with conventional e-beam systems [11]. However, use of two in-line vapor targets and the gas jet could quite conceivably overcome this troublesome problem by mixing the two vapor plumes for efficient, compositionally correct deposition (Fig 11.1). Incorporation of a high rate scanning system into the current DVD configuration would allow the beam power to be precisely split between the two targets for stoichiometrically-correct evaporation [236]. Additional research will need to be conducted to investigate the deposition rate around fibers for different elements, since as noted in the Background chapter, the non-line-of-sight coating efficiency of low vacuum systems is a function of the mass of the chamber gas and the vapor atoms. No data currently exists which explains how to obtain a stoichiometrically correct Ti-6-4 deposit in a DVD system.

12.4 Enhanced Energy Deposition

Point four of Chapter 3 suggested that DVD could possess an ability to deposit atoms onto substrates with energies above their initial 0.2 eV thermal levels. The modeling work of Chapters 8 - 11 strongly suggests that the supersonic carrier gas stream cannot achieve this

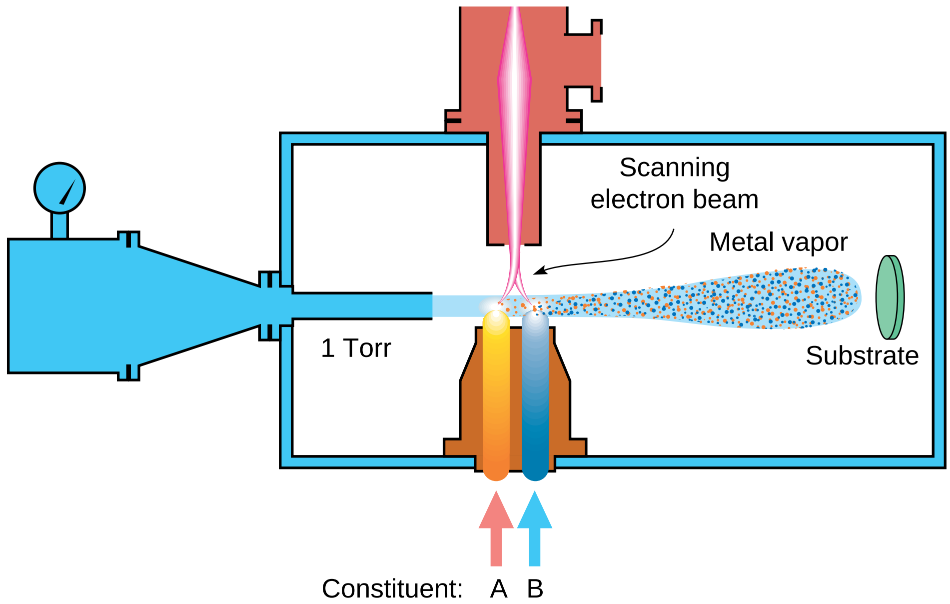

Figure 12.1 **Multicrucible vapor stream mixing in DVD.** Stoichiometrically-correct deposition using this DVD system configuration could be much faster and more efficient than that achieved in a conventional multicrucible e-beam evaporation system (c.f. Fig. 2.1).

goal for the system configurations examined. Fig. 9.6 shows that the model is capable of predicting with reasonable accuracy the vapor atom energy changes as the result of collisions with a background gas, and Fig. 10.4 suggests that for some DVD flow conditions the vapor atoms are temporarily accelerated to energies above thermal limits. However, it appears reasonable to believe that these model results are correct when they predict that the temporarily high energy levels are not sustained, most often because of the wall jet which rapidly slows vapor atoms prior to contact with the substrate. Since the system does not demonstrate an ability to enhance depositing atom energy, there is no reason to believe that point five, an increased possibility of athermal atomic reconstruction at the growth surface, will be satisfied either.

Even when the system is reconfigured as in Chapter 11, it is not possible to generate flow conditions which deposit vapor atoms with 1 - 2 eV. To accelerate the vapor atoms in a DVD system it certainly appears that some other mechanism must be employed to generate high energy deposits. Substrate biasing designed to pull in the ionized vapor atoms appears to be a logical system enhancement which might achieve this goal.

Despite deposition energies well below initial thermal levels, research by Hass et al. [217] suggests that there are important applications like the thermal barrier coating of aircraft engine turbine blades for which DVD could be an ideal deposition tool. The TBC application requires high rate, efficient deposition of low energy columnar microstructures (Fig. 2.8 a) composed of refractory alloys and compounds with elements having significantly different vapor pressures. Although a significant amount of development work needs to occur before DVD might be adopted by industry for the TBC application, this seems to be a second promising application area for the technology.

12.5 Rapid, Continuous Processing of Pure Materials and Compounds

The final three points of Chapter 3 propose that DVD could be capable of rapid, continuous processing of pure materials and compounds. The experimental work of Chapter 6 and the subsequent efforts of Hass et al. [217] encouragingly indicate that DVD can deposit both pure materials and compounds from its low vacuum environment. The major problem with the system configuration visualized in Chapter 5 is the variability of vapor stream location with e-beam power and thus material evaporation rate. Industrial systems are almost certainly going to have to be configured to eliminate this variability. There is some reason to believe that the system reconfiguration proposed in Chapter 11 will largely diminish the problem since vapor atom travel to the substrate will not depend upon significant numbers of carrier gas/vapor atom collisions for 90^o redirection. Since the model cannot examine transport effects resulting from a change in vapor atom flux density, the level of deposition distribution variation with changes in density cannot be examined.

Although continuous processing was not attempted in the research DVD system constructed, there appears to be little to suggest why continuous batch processing (e.g. individual turbine blades) through load-locks or continuous material feed (e.g. continuous fiber) through differentially pumped material introduction chambers should not be possible [186]. If industry decides to develop the technology, these issues should be resolved quickly.

12.6 Other Applications

In this dissertation, exploration of DVD's ability to manufacture films useful for other applications has been limited. However, DVD's ability to create films using reactive deposition techniques and the ability to create polycrystalline silicon at temperatures compatible with glass substrates (Chapter 6) suggests that, with further development, DVD might be applied to the microelectronics application area (e.g. thin film transistor silicon substrates). The major drawback at present for the use of DVD in the microelectronics industry appears to be the system's inability to produce fully dense film coatings. While Chapter 11 suggests ways in which a system reconfiguration could create higher energy deposits by substrate biasing or ion bombardment, there is no experimental evidence available demonstrating that such a DVD system produces a fully dense film. Since DVD already generates many excited and ionized vapor atoms, it is appealing to consider using this feature of the system for some film creation benefit. Use of DVD for the synthesis of microelectronic materials could require a lower accelerating voltage to minimize harmful x-ray generation. Conveniently, use of a lower accelerating voltage appears feasible in a system configured according to the ideas presented in section 11.1 in which chamber pressures are in the milliTorr (1 Pa) range. The lower processing chamber pressures of this system are compatible with lower accelerating voltages (equation (4.2) and Fig. 4.1) and with ion bombardment systems should such additional tools prove necessary.

12.7 Other System Configurations

The experimental work of Chapters 5 - 7 demonstrates that, for applications other than fiber coating, the current DVD system configuration has several important design flaws. The most important of these is the variation in material deposition characteristics with changes in e-beam power (Figs. 5.10 and 5.11). Industry almost certainly will demand that the process provide a more consistent processing environment, not one which requires increasing amounts of carrier gas to bend the vapor stream towards the substrate as the e-beam gun power is raised while simultaneously decreasing material utilization efficiency.

The modeling results of Chapter 11 suggest that it could be possible to reconfigure the DVD system in a manner which will yield more consistent results. However, before industry will adopt DVD in such a configuration, the capabilities of a reconfigured system must be demonstrated in the lab or a more sophisticated model must be developed which is capable of simulating the effect of various vapor atom flux densities upon DVD deposition characteristics.

12.8 Summary

A great deal of effort has already been invested in the development of Directed Vapor Deposition. However, as suggested in this chapter, a great deal more work must be done before industry will be convinced that the technology represents a well-understood tool capable of creating products with desired microstructures and properties.