Chapter 6

Materials Synthesis Via Directed Vapor Deposition

6.1 Overview

Experimental work was undertaken to explore the ability of Directed Vapor Deposition to synthesize a variety of films in a low vacuum environment. Although extensive examination of specific material system applications will be left to future research, several sets of initial experiments were conducted to define the abilities of DVD to synthesize useful film structures. These investigations examined the ability of DVD:

- To deposit pure elements, without significant oxygen contamination from the carrier gas flow.
- To evaporate silicon for the creation of polysilicon films on glass substrates at substrate temperatures below 600°C.
- To deposit metal oxides reactively by evaporating pure metal sources and entraining oxygen in the carrier gas stream.

Fig. 6.1 shows the general geometric configuration of the DVD system for all experiments described in this chapter.
6.2 Contamination Study of Nonreactive Deposition

As noted in the Background chapter (section 2.1.3.), one of the major concerns in the scientific community regarding low vacuum vapor phase processing centers around the incorporation of contaminants into the deposited film from the gas in the chamber. To assess the ability of DVD to create clean, pure material deposits, copper (99.999% pure) and titanium (99.99% pure) obtained from ESPI (Ashland, OR) were separately deposited and the concentration of oxygen measured in each resulting film. For these studies, films approximately 80 µm thick were deposited in 30 minutes at a deposition rate of 2-3 µm/min. The substrate temperature was maintained at 200°C by substrate heaters. E-beam scanning was not employed for either deposition experiment. Instead, a fixed beam with a power of 1.5 kW was used throughout. A 10 slm purified helium gas flow was used to entrain vapor, and the processing chamber pressure was set at 95 Pa (~ 0.7 Torr) with a
mixing chamber pressure of 425 Pa (~ 3.2 Torr). These conditions resulted in deposition at a nominal Mach number of 1.58 through the 1.27 cm diameter nozzle.

In collaboration with P. Ratnaparkhi, the films were analyzed following deposition using Auger electron spectroscopy (AES) which has an oxygen detection limit of 0.1 atomic percent. After being introduced into the high vacuum Auger analysis chamber (P < $10^{-8}$ Torr), the samples were sputter cleaned in situ for a minimum of 45 minutes using a 3 keV argon beam to remove surface contaminants. Sputter rates were estimated to be about 400 nm/min for copper and about 200 nm/min for titanium. Once sputter cleaning had been completed, chemical analysis was immediately performed at electron beam energies of 3 and 5 keV.

Auger electron spectroscopy detects atomic composition close to the surface of a sample (within a few nanometers) through detection of a three electron process [205]. The initial incident electron, in this case an electron possessing 3 or 5 keV of kinetic energy, interacts with an atom near the sample surface and ejects an inner shell electron of that atom. Almost immediately the resulting inner electron shell hole of the atom is filled by an outer shell electron falling in to fill the gap. When the outer shell electron falls, it gives off energy, equal to the energy difference between its original shell and final shell positions. The energy released via this transition then either leaves the sample directly as an x-ray (the basis for x-ray photoelectron spectroscopy) or interacts with another outer shell electron which is subsequently ejected from the atom. The energy of this final ejected electron is what an AES system detects. The kinetic energy of the ejected Auger electron depends upon the specific element and intershell transition which generated it, allowing for electrons ejected from copper or titanium to be differentiated from those ejected from oxygen or carbon.
An Auger scan obtained from this study shows the signal detected from a copper sample containing little oxygen contamination (Fig. 6.2). The auger analysis did not detect an oxygen signal which would have appeared at an energy of about 506 eV had more than 0.1 at. % of oxygen been present in the film. An extended Auger scan which focussed on the energy range around 506 eV and around the copper peaks allowed oxygen and carbon content of the copper films to be quantified at less than the detection limit of 0.1 at. % (equivalent to 1000 parts per millions (ppm)). For the titanium sample, auger analysis similarly indicated that oxygen incorporation into the titanium film during DVD processing was less than 1000 ppm [203]. The results of this section indicate that engineering films with low oxygen contamination levels can be created using Directed Vapor Deposition even though the technique operates at pressures above $10^{-3}$ Torr in the material synthesis chamber.

The analysis leaves unanswered the question of inert carrier gas incorporation into DVD films. Auger analysis cannot detect helium since helium has only two electrons. It seems unlikely though that neutral, inert helium would have any significant probability of bonding to the depositing film surface. However, the visualization studies of Chapter 4 suggest that there are excited and possibly ionized helium gas atoms in the chamber. The probability of these atoms binding to the film surface long enough to become incorporated into the film is not easily determined.

### 6.3 Study of Silicon Deposition

As a first attempt to investigate the ability of DVD technology to deposit a semiconducting material, a study of silicon deposition was undertaken. Silicon was deposited upon glass substrates to assess the quality and type (i.e. amorphous or polycrystalline) of microstructure created [206, 207]. For these experiments, a 5.08 cm diameter by 2.54 cm long, solid, phosphorous-doped (0.1 Ω-cm), single-crystal silicon ingot was used as the evapo-
The material was obtained from Virginia Semiconductor (Fredericksburg, VA). Due to the dimensions of the source material, it was not placed inside the crucible for evaporation. Instead it was set on a platform uncontained by any cooling apparatus.

Two runs were performed using helium as the carrier gas. The first run deposited silicon in a chamber maintained at 150 Pa (1.1 Torr) with a carrier gas Mach number of 1.5 (pressure ratio = 4.2) and a helium flow rate of 40 slm while the second run deposited material in a chamber pressure of 13 Pa (0.1 Torr) at a Mach number of 2.8 (pressure ratio = 26) and a helium flow rate of 5 slm. The 40 slm run made use of the 1.27 cm diameter nozzle to achieve its pressure conditions while the 5 slm run employed the 0.85 cm diameter noz-

Figure 6.2 An Auger electron spectroscopy scan of DVD deposited copper. This AES scan reveals little or no oxygen contamination in the deposited copper film.
zle. An unscanned electron beam with a power of 240 - 480 W was used to evaporate the silicon while stationary, unheated glass substrates were used to collect the deposit. The experimental system configuration was the same as shown previously in Fig. 7.1 for the deposition efficiency studies.

Initially, attempts were made to increase the e-beam power as a means of raising the silicon deposition rate. These attempts with an unscanned e-beam proved unsuccessful, with higher power runs leading to severe cracking of the silicon source material, highlighting the distinctly different evaporation behavior of a material like silicon when compared to a more thermally conductive material like copper. Study of thermal conductivity indicates that at 373.2 K copper has a thermal conductivity of 3.95 W/(cm K) while silicon has a conductivity of 1.08 W/(cm K) [208]. Since the silicon is unable to dissipate energy through heat conduction as rapidly as copper, it appears to disperse at least some of the e-beam’s energy via the formation of free surfaces (cracks) in the source material. At the time that these experiments were undertaken, the e-beam scanning system was not installed in the DVD system. Thus it was not immediately possible to develop a beam scan pattern with a high frequency scanning system to spread the e-beam power over the surface of the source material. Such an alteration should make possible higher rate evaporation and deposition of materials which are not as conductive as copper.

Optical transmission and reflection analysis of the deposited silicon films was undertaken by T. Globus to determine the silicon film form (amorphous or polycrystalline), the film thickness, and the average material deposition rate [209]. Measurements in the 0.6 - 2.4 μm energy wavelength range were made using a Cary 5E two-beam spectrophotometer. Film thicknesses were calculated from interference fringe patterns observed in the weak absorption portion of the visible spectrum. Deposition rates ranging from 20 to 440 nm/min were calculated. The highest rate was recorded from the 40 slm sample created.
using 480 W of beam power. The thickest 3.1 µm film was deposited in 7 minutes over an area of approximately 6.45 cm². The optical transmission spectra from several films were used to calculate the thin film absorption spectrum shown in Fig. 6.3. The absorption spec-

![Optical absorption coefficient analysis of DVD deposited silicon.](image)

Figure 6.3 **Optical absorption coefficient analysis of DVD deposited silicon.** The optical absorption coefficient as a function of photon energy for DVD silicon is distinctly different than that reported in the literature [210, 211] for hydrogenated amorphous silicon (a-Si, H) and crystalline silicon (c-Si).

trum for single crystal silicon and PECVD hydrogenated amorphous silicon (15% hydrogen) are also included for comparison.

The absorption edge for the DVD amorphous silicon (a-Si) thin films is shifted to lower energies relative to the PECVD hydrogenated amorphous silicon (i.e., a-Si, H in Fig. 6.3)
because the DVD material is not an \(a\)-Si:H alloy. As a result, the photon energy absorption characteristics of the DVD material are quite similar to those of crystalline silicon for energies greater than 1.4 eV. This agreement of the DVD silicon results with the crystalline silicon, as opposed to the hydrogenated amorphous silicon absorption characteristics, does not necessarily indicate that polycrystalline silicon has been formed. Instead the similarity is generated by the dangling bonds in the DVD amorphous silicon which are not passivated (by hydrogen) and which lead to a large density of near bandgap edge states\(^1\).

Using the technique of Amer and Jackson [211], the concentration of these bandgap edge state defects was estimated to be \(10^{18}\) cm\(^{-3}\). For comparison, the typical defect density in evaporated nonhydrogenated \(a\)-Si is approximately \(10^{19} - 10^{20}\) cm\(^{-3}\) [212]. While the defect density result suggests that the DVD deposit is different than a typical nonhydrogenated \(a\)-Si film and the absorption spectrum shows it to be different than hydrogenated amorphous silicon, these results do not establish the crystallinity of the deposits.

Microstructural analysis of the films created by these deposition runs was performed by L. Hsiung to understand the form of these films further [213]. Analysis of the 3.1 \(\mu\)m thick, 40 slm sample revealed silicon atom clusters ranging from 20 to 300 nm in size and surrounded by microvoids. The material porosity was estimated to be 1.0\%. Selected area diffraction (SAD) performed on this film indicated that it was completely amorphous. Similar analysis on the Mach 2.6 samples revealed several microcrystalline structures, suggesting that some crystalline nucleation can be achieved in the DVD system even at

\(^{1}\) Hydrogenated silicon experiments were not carried out due to concerns about the safety of flowing hydrogen through the DVD pumping systems. However, there is no technical barrier to conducting such experiments once safety concerns are properly addressed.
room temperature. This initial result is encouraging for the future deposition of low-temperature polycrystalline silicon.

Following the completion of this initial series of silicon deposition via e-beam DVD, a more extensive study was undertaken with Ritenour [214]. Ritenour’s study investigated the effect of substrate temperature, jet composition (argon and helium), and e-beam power upon amorphous and polycrystalline silicon formation. For deposition rates of 150 - 300 nm/min (e-beam power = 360 - 420 W), Ritenour observed a transition from amorphous to polycrystalline microstructure at a substrate temperature in the range of 475 - 515°C. The determination of crystallinity was made via a comparison of the optical absorption spectra for DVD silicon to that of crystalline silicon, similar to Fig. 6.3. For all silicon films deposited at temperatures above 300°C, a rough surface morphology considered unsuitable for electronic applications was observed via scanning electron microscopy. Amorphous silicon films deposited on a 70°C substrate at a higher deposition rate (e-beam power = 600 W) exhibited less surface roughness. For deposition runs performed under similar DVD process conditions, the addition of 5% argon to the jet was found to increase the film roughness. The details of Ritenour’s more detailed study, found in [214, 215], extend the findings of the initial silicon deposition study reported here. A portion of Ritenour’s results are summarized in Table 6.1. It certainly appears that under certain DVD process conditions it does appear that crystalline silicon depositing is feasible.

The results of this section indicate that while the microstructure of deposited silicon films needs to be improved through an elimination of internal porosity and a decrease in film surface roughness, Directed Vapor Deposition could have the ability to deposit polycrystalline silicon at temperatures compatible with the glass substrates used to create thin film transistors for use in devices such flat panel displays. If the DVD process can be modified
to improve deposited film quality, it could prove to be a useful tool for this industrial application.

Table 6.1: DVD deposition of silicon

<table>
<thead>
<tr>
<th>Substrate Temperature (°C)</th>
<th>E-beam Power (W)</th>
<th>Resulting Microstructure</th>
</tr>
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<tbody>
<tr>
<td>70¹</td>
<td>600²</td>
<td>Amorphous. Generally smooth morphology, repeated domed regions ~0.35 µm in diameter, no clear separation between adjoining domes. Film cracking evident. Optical appearance = grey.</td>
</tr>
<tr>
<td>325</td>
<td>480</td>
<td>Amorphous. Distinct columns ~0.25 µm in diameter, clear void spaces between columns, rough surface morphology. Optical appearance = grey.</td>
</tr>
<tr>
<td>425</td>
<td>360</td>
<td>Amorphous. Distinct columns ~0.25 µm in diameter, clear void spaces between columns, rough surface morphology. Optical appearance = grey.</td>
</tr>
<tr>
<td>475</td>
<td>420</td>
<td>Amorphous. Distinct columns ~0.25 µm in diameter, clear void spaces between columns, rough surface morphology. Optical appearance = grey.</td>
</tr>
<tr>
<td>515</td>
<td>420</td>
<td>Polycrystalline. Larger diameter columns ~0.33-0.50 µm in diameter, less obvious separation, continued rough surface morphology. Optical appearance = silver.</td>
</tr>
<tr>
<td>550</td>
<td>300</td>
<td>Polycrystalline. Larger diameter columns ~0.33-0.50 µm in diameter, less obvious separation, continued rough surface morphology. Optical appearance = silver.</td>
</tr>
</tbody>
</table>

¹ Condensation of the silicon vapor increased the substrate temperature from room temperature to 70°C.

² Deposition rate for this experiment exceeded the deposition rate used in other experiments.
6.4 Study of Reactive Deposition

While an ability to deposit pure metallic and semiconducting materials using Directed Vapor Deposition (DVD) is critical, another proposed area of DVD utility is the creation of compounds through the combination of solid materials with elements in the carrier gas flow. Since DVD introduces gas into the film synthesis chamber as part of normal processing, it appears to be a method well suited to the stoichiometrically-correct creation of compounds from either compound evaporant targets [216] or pure metal targets [200]. Research by others with conventional e-beam evaporators [11] has shown that during evaporation and deposition of compounds (e.g. zirconia for thermal barrier coatings), the stoichiometry of deposited films is frequently incorrect, most often the result of reactive element loss (e.g. oxygen) to the gas phase. To make up for this deficiency, process engineers have performed material deposition in a low pressure of the desired gaseous element (RE and ARE are described in the Introduction).

It should be possible to introduce reactive gas into the DVD carrier gas stream to ensure stoichiometrically-correct deposition from solid compound sources. Using the carrier gas jet of the DVD system it should also be possible to introduce all of the reactive elements into the system from the gas phase. If this approach proves successful, it will be possible to avoid the use of difficult to evaporate ceramic rods, which frequently crack in a manner similar to the silicon rods described above, and to evaporate instead from more controllable metal or alloy sources. To assess the ability of the Directed Vapor Deposition system to deposit material onto flat substrates following reaction between the vapor stream and a gas stream containing oxygen, a limited study was undertaken.

An initial experimental study of reactive DVD deposition was undertaken with Heller [200]. For this study of reactive deposition feasibility, deposition of zirconia (ZrO$_2$) was
investigated by evaporating pure zirconium metal from the water-cooled crucible and then introducing oxygen into the carrier gas/metal vapor flow downstream of the crucible via a separate gas injection subsystem as illustrated in Fig. 4.7. Ideally, reaction between the zirconium and oxygen should occur and lead to deposition of an oxide coating.

Only a few coatings were created using this system configuration and limited analysis of the samples was undertaken. Still, a marked change in the color of the excited vapor stream during deposition from a faint silver to a bright white was observed when oxygen was introduced into the system, suggesting that a reaction was occurring between the metal and oxygen. In addition, visual comparison of metallic zirconium deposits which were black or silver contrasted strongly with the white color of the reactively deposited material [200]. In subsequent studies of DVD reactive deposition in which a partial pressure of oxygen was introduced into the primary carrier gas flow, Hass et al. [217] have confirmed, via x-ray diffraction analysis, that DVD can deposit white zirconia films by evaporating pure zirconium into a reactive gas jet.

The oxide deposition tests performed with this system configuration quickly revealed that, while DVD appeared to have an ability to synthesize reactive films by evaporating pure materials into a reactive gas environment, the perpendicular injection of the oxygen stream into the carrier gas/vapor stream (the gas injection system shown to the right of the crucible in Fig. 4.7) significantly disrupted the flow of vapor toward the substrate. Rather than allowing the jet to continue to travel towards the substrate with oxygen added to the vapor-laden stream, the perpendicular orientation of the oxygen flow injection forced the inert gas/metal vapor stream from a horizontal into a generally vertical orientation well in front of the substrate, similar to the effect experiences as a result of jet interaction with the crucible (Fig. 5.12 c)). Although reaction and reasonable mixing appeared to be occurring, deposition rates were significantly reduced [200]. This disruption of the
primary gas and vapor flow was deemed unacceptable because of its apparent detrimental effect upon adatom deposition efficiency and energy. Since the DVD system also allows reactive gas elements to be added in precise quantities to the inert gas flow in the mixing chamber using the mass flow controllers (c.f. Fig. 4.10), it appears that the greatest success in DVD reactive deposition will occur when a reactive gas jet is passed through the nozzle and into the chamber for more predictable reactive deposition as Hass et al. have more recently done [217].

This section’s results show that DVD can use reactive deposition techniques to deposit compound films.

6.5 Concluding Remarks

The creation of uncontaminated films and compound films via reactive deposition has demonstrated an important ability of the Directed Vapor Deposition technique, selective incorporation of useful gas phase elements into film deposits. DVD’s demonstrated ability to deposit pure coatings of highly reactive titanium, combined with the method’s enhanced fiber coating material utilization efficiency, show that this vapor deposition technology should be considered as a method for creating continuous fiber reinforced MMCs. More research needs to be conducted before the utility of DVD reactive deposition or DVD polysilicon creation can be fully assessed. However, the initial results reported here suggest that with continued system development, DVD’s reactive deposition abilities could contribute to useful TBC synthesis [217], and DVD’s ability to deposit polysilicon at temperatures compatible with glass substrates could motivate system modifications which make possible electronic material synthesis via DVD.