Chapter

1

Thin-Film Technology

1.1 Applications

Thin films are deposited onto bulk materials (substrates) to achieve properties unattainable or not easily attainable in the substrates alone. Thus, the first question to ask is, "What properties are required for the application at hand?" Table 1.1 divides these properties into five basic categories and gives examples of typical applications within each category. Examination of this table shows that the range of thin-film applications is very broad indeed. Often, multiple properties are obtainable simultaneously. For example, Cr coatings used on plastic parts for automobiles impart hardness, metallic luster, and protection against ultraviolet light. Titanium nitride (TiN) coatings on cutting tools offer hardness, low friction, and a chemical barrier to alloying of the tool with the workpiece (galling). They also offer a rich, gold color for decorative applications. The Cr coating on a plastic part achieves the functionality of the same part made from bulk metal, but at significant savings in cost and weight. The TiN coating achieves surface properties unattainable in a bulk material, since the bulk material must also offer high strength and toughness in the cutting tool application.

Additional functionality in thin films can be achieved by depositing multiple layers of different materials. Optical interference filters consist of tens or even hundreds of layers alternating between high and low indexes of refraction. When alternating layers are made using nanometer thicknesses of semiconducting materials such as GaAs and (AlGa)As, the result is a "superlattice" that has electrical properties governed by the constructed periodicity rather than by the atomic

TABLE 1.1 Thin-Film Applications

Thin-film property category	Typical applications
Optical	Reflective/antireflective coatings Interference filters Decoration (color, luster) Memory discs (CDs) Waveguides
Electrical	Insulation Conduction Semiconductor devices Piezoelectric drivers
Magnetic	Memory discs
Chemical	Barriers to diffusion or alloying Protection against oxidation or corrosion Gas/liquid sensors
Mechanical	Tribological (wear-resistant) coatings Hardness Adhesion Micromechanics
Thermal	Barrier layers Heat sinks

periodicity. Thus, multilayer thin films can behave as completely new, engineered materials unknown in bulk form. When multiple layering is combined with lithographic patterning in the plane of the films, microstructures of endless variety can be constructed. This is the basic technology of the integrated-circuit industry, and more recently it is being applied to optical waveguide circuitry and to micromechanical devices. The latter include such creations as rotary electrostatic motors tens of micrometers in diameter, which is a clear case of a device awaiting an application.

This book will examine the deposition of thin films from the vapor phase. Omitted will be the deposition of thick films as well as deposition from the liquid phase. The distinction between thin-film and thick-film technology is that the former involves deposition of individual molecules, while the latter involves deposition of particles. Examples of thick-film techniques are painting, silk screening, spin-on glass coating, and plasma spraying. The thick-film techniques are important and relatively inexpensive, but they do not offer the control or the material quality of the thin-film techniques. Note that films deposited

by a thin-film technique can be thicker than those deposited
thick-film technique, such as graphite plates several millimeters
deposited by thermal decomposition (pyrolysis) of hydrocarbon va
Also omitted here will be films grown by reaction with the subs
rather than by deposition, such as silicon dioxide grown by the
mal reaction of water vapor with Si.

The vapor phase thin-film techniques have three significant ad
tages over the liquid-phase techniques: applicability to any mat
wide adjustability in substrate temperature, and access to the su
during deposition. Temperature is a key variable in altering film
erties. Access to the surface allows energy to be delivered by ion
bardment and allows surface analysis during deposition. We wil
in Chap. 8 that ion bombardment can alter film properties dra
cally. Surface analysis by electron diffraction during depositio
been central to research on epitaxial (single crystal) film gr
behavior. Regarding the liquid-phase techniques, liquid-phase ep
is useful for low-cost production but does not have the control o
Chap. 6 processes. Electroplating from liquid solution is widely
occasionally even for epitaxy. However, its technology is very diff
from the vapor-phase techniques to be examined here.

1.2 Process Steps

All thin-film processes contain the four (or five) sequential s
shown in Fig. 1.1. A source of film material is provided, the materi
transported to the substrate, deposition takes place, sometimes
film is subsequently annealed, and finally it is analyzed to eval
the process. The results of the analysis are then used to adjust
conditions of the other steps for film property modification. Additi
process control and understanding are obtained by monitoring
first three steps during film deposition. In subsequent chapters,
of the deposition processes will be discussed in terms of the s
shown in Fig. 1.1, and various techniques for monitoring and cont
ling these steps will be examined. Annealing will not be discus
except to the extent that it occurs during deposition. Post-deposi
annealing can be used to activate grain growth, alter stoichiome
introduce dopants, or cause oxidation. However, this book conf
itself to the deposition process itself. Below, we briefly elaborate on
steps shown in Fig. 1.1.

The **source** of the film-forming material may be a solid, liq
vapor, or gas. Solid materials need to be vaporized to transport th
to the substrate, and this can be done by heat or by an energetic be
of electrons, photons (laser ablation), or positive ions (sputteri
These methods are categorized as *physical* vapor deposition (PV

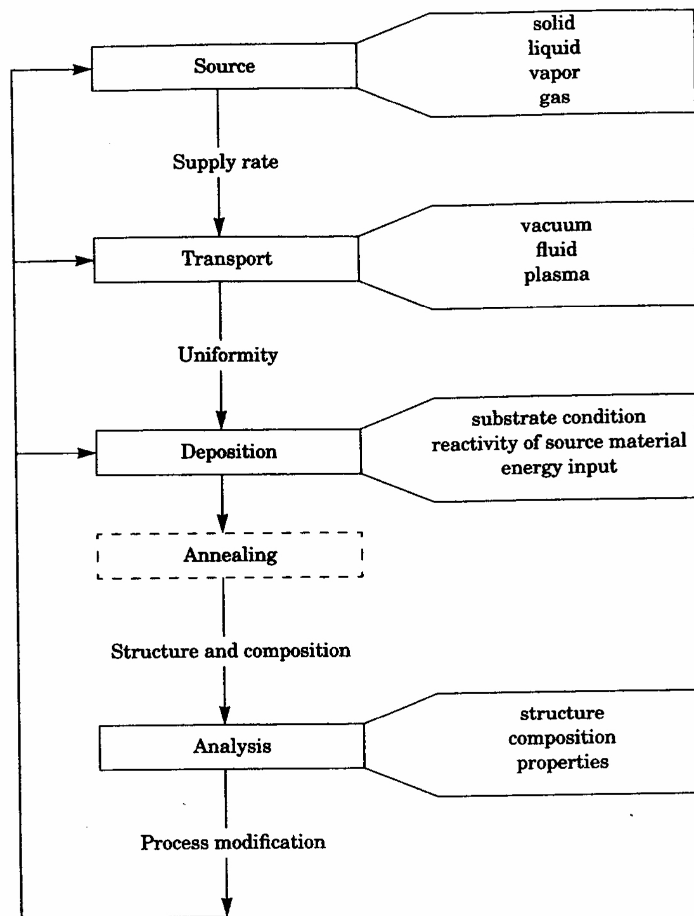

Figure 1.1 Thin-film process steps. In all steps, process monitoring is valuable, and contamination is a concern.

Occasionally, solid sources are instead *chemically* converted to vapors, such as Ga to GaCl. In other cases, the source material is supplied as a gas or as a liquid having sufficient vapor pressure to be transported at moderate temperatures. Thin-film processes that use gases, evaporating liquids, or chemically gasified solids as source materials are categorized as *chemical* vapor deposition (CVD). In both PVD and CVD, contamination and supply rate are the major source-material issues. Contamination is also an issue in the transport and deposition steps.

Supply rate is important because film properties vary with deposition rate and with the ratio of elements supplied to compound films.

In the **transport** step, the major issue is uniformity of arrival rate over the substrate area. The factors affecting this uniformity are very different, depending on whether the transport medium is a high vacuum or a fluid. (Here we are talking about gaseous fluids rather than liquid fluids.) In a high vacuum, molecules travel from the source to the substrate in straight lines, whereas in a fluid there are many collisions among molecules during the transport step. Consequently, in a high vacuum, uniformity of source-material arrival rate at the substrate is determined by geometry, whereas in a fluid it is determined by gas flow patterns and by diffusion of the source molecules through the other gases present. Often, the high-vacuum processes are equated with physical vapor deposition, and the fluid-flow processes are equated with chemical vapor deposition. However, this is not always a valid association. Although many physical deposition processes do operate in a high vacuum, others like laser ablation and sputtering often operate at higher pressures characteristic of a fluid. Similarly, although most chemical deposition processes operate at fluid pressures, chemical beam epitaxy operates in a high vacuum.

The high-vacuum transport medium has the important advantage of clear access to the deposition surface. This allows energy input from an ion beam and allows the use of analytical techniques involving electron beams, such as electron diffraction and Auger spectroscopy. On the other hand, the fluid medium has the advantage that it functions at atmospheric pressure or at easily-achieved moderate vacuum levels. In both media, contamination can be dealt with equally well and using similar techniques.

Many thin-film processes operate in a plasma, which is listed in Fig. 1.1 as a third transport medium. A plasma is a partially ionized gas and is often regarded as the fourth state of matter (solid, liquid, gas, and plasma). Plasmas contain a great deal of energy, which can activate film deposition processes at low temperature. The plasma operating pressure can be such that it behaves either as a fluid or as a high-vacuum medium.

The third step in the thin-film process is the actual **deposition** of the film onto the substrate surface. Deposition behavior is determined by source and transport factors and by conditions at the deposition surface. There are three principal surface factors which determine the deposition behavior, as seen in Fig. 1.1. These factors are substrate surface condition, reactivity of the arriving material, and energy input. Substrate surface condition includes roughness, level of contamination, degree of chemical bonding with the arriving material, and crystallographic parameters in the case of epitaxy. The reactivity

factor refers to the probability of arriving molecules reacting with the surface and becoming incorporated into the film. This probability is known as the "sticking coefficient," S_c, and it can vary from unity to less than 10^{-3}. It is generally lower for CVD than for PVD processes, and low S_c aids in coating convoluted shapes and in deposition on selected areas.

The third deposition factor is energy input to the surface. It can come in many forms and has a profound effect on both the reactivity of arriving material and on the composition and structure of the film. Substrate temperature is the basic source of energy input, but there are many other sources. Photons are used in photoassisted and laser-assisted deposition. Positive ion bombardment carries very large amounts of energy. It is present in most plasma processes and in some high-vacuum processes. Chemical energy is carried by inherently reactive source molecules and by molecules that have been dissociated in the course of vaporization or plasma transport. In summary, the three deposition factors of substrate condition, reactivity, and energy input work together with the arriving fluxes to determine the structure and composition of the deposited film. The structure and composition in turn determine the various film properties listed in Table 1.1.

The final step in the deposition process is **analysis** of the film. One level of analysis consists of directly measuring those properties that are important for the application at hand, such as the hardness of a tool coating, the breakdown voltage of an insulator, or the index of refraction of an optical film. Many film deposition processes are optimized using the empirical approach of measuring key film properties as a function of the process variables that can be varied in the first three steps of the deposition. This approach is suggested by the "feedback" arrows in Fig. 1.1. A deeper level of analysis involves probing the film's structure and composition, since those are the factors that determine the observed properties. This type of analysis is generally more difficult, but it provides a bridge between the deposition step and the final film properties. This bridge leads to a better understanding of the overall process.

Analysis of the film after deposition can be thought of as the final stage of process monitoring. Monitoring is important at all steps in the thin-film process. The more monitoring that can be done during deposition, the better will be both the control and the understanding of the process. For example, the supply rate of each source material can be continuously metered and feedback-controlled. The composition of the transport medium can be analyzed for both reactant concentration and contaminants. Both the deposition rate and the film crystallography can be monitored in real time. Throughout this book, techniques

for process monitoring will be introduced as appropriate for each de-position method.

1.3 Conclusion

This introductory chapter has presented many concepts in a gene[ral] way to give the reader an overview and to provide a framework wit[h] which to discuss specific deposition techniques. These concepts m[ay] seem somewhat abstract at present, but they will take on more s[ub]stance in the context of later discussion. It will be useful to refer b[ack] to this chapter from time to time, especially to Fig. 1.1, to see m[ore] clearly the parallels between the various deposition techniques and develop a sense of the underlying principles which unify thin-f[ilm] technology.

1.4 Exercise

1.1 List as many thick-film or thin-film applications as you can fr[om] among familiar industrial or consumer products. For each, list t[he] properties required for the film to function effectively.