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L. B. Freund and S. Suresh
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Introduction and Overview

Thin solid films have been used in many types of engineering systems and have been adapted to fulfill a wide variety of functions. A few examples follow.

- Great strides in thin film technology have been made in order to advance the rapid development of miniature, highly integrated electronic circuits. In such devices, confinement of electric charge relies largely on interfaces between materials with differing electronic properties. Furthermore, the need for thin materials of exceptionally high quality, reproducible characteristics and reliability has driven film growth technology through a rapid succession of significant achievements. More recently, progress in the physics of material structures that rely on quantum confinement of charge carriers continues to revolutionize the area. These systems present new challenges for materials synthesis, characterization and modeling.
- The use of surface coatings to protect structural materials in high temperature environments is another thin film technology of enormous commercial significance. In gas turbine engines, for example, thin surface films of materials chosen for their chemical inertness, stability at elevated temperatures and low thermal conductivity are used to increase engine efficiency and to extend significantly the useful lifetimes of the structural materials that they protect. Multilayer or continuously graded coatings offer the potential for further progress in this effort.
- The useful lifetimes of components subjected to friction and wear due to contact can be extended substantially through the use of surface coatings or surface treatments. Among the technologies that rely on the use of thin films in this way are internal combustion engines, artificial hip and knee implants, and computer hard disks for magnetic data storage.
- Thin films are integral parts of many micro-electro-mechanical systems designed to serve as sensors or actuators. For example, a piezoelectric or

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piezoresistive thin film deposited on a silicon membrane can be used to detect electronically a deflection of the membrane in response to a pressure applied on its surface or by an acceleration of its supports. Devices based on thin film technology are used as microphones in hearing aids, monitors of blood pressure during exercise, electronically positioned thin film mirrors on flexible supports in optical display systems, and probes for detecting the degree of ripeness of fruits.

Numerous other technologies rely on thin film behavior. An immediate observation that follows from the foregoing list is that the principal function of the thin film components in these applications is often not structural. Consequently, load-carrying capacity may not be a principal consideration for design or material selection. However, fabrication of thin film configurations typically results in internal stress in the film of a magnitude sufficient to induce mechanical deformation, damage or failure. A tendency for stress-driven failure of a thin film structure can be a disabling barrier to incorporation of that film into a system, even when load-carrying capacity is of secondary importance as a functional characteristic. The presence of an internal stress in a thin film structure may also influence the electrical or magnetic properties in functional devices.

This chapter provides an overview of commonly used deposition and processing methods for the synthesis and fabrication of thin film structures. This is followed by a discussion of the fabrication of small volume structures, where examples of the basic steps involved in lithography, surface micromachining, bulk micromachining and molding processes are considered in the context of the manufacture of microelectronic devices, as well as small structures encountered in the development of micro-electro-mechanical systems (MEMS) and nano-electro-mechanical systems (NEMS). Attention is devoted to the effects of processing on the nucleation and growth of monocrystalline and polycrystalline thin films on substrates, the evolution of film microstructure in polycrystalline films, and the generation of internal stresses through processing. In the chapters that follow, consequences of stress in thin film and multilayer materials are studied, organized according to the deformation or failure phenomena that can be induced by internal stress.

1.1 A classification of thin film configurations

As a guide for the development and application of concepts that are useful for describing mechanical behavior of solid thin film and multilayer materials, it is convenient to classify structures in terms of their geometrical configurations and the nature of constraint on their deformation imposed by their surroundings. For this purpose, configurations are classified in terms of the relative extent of the

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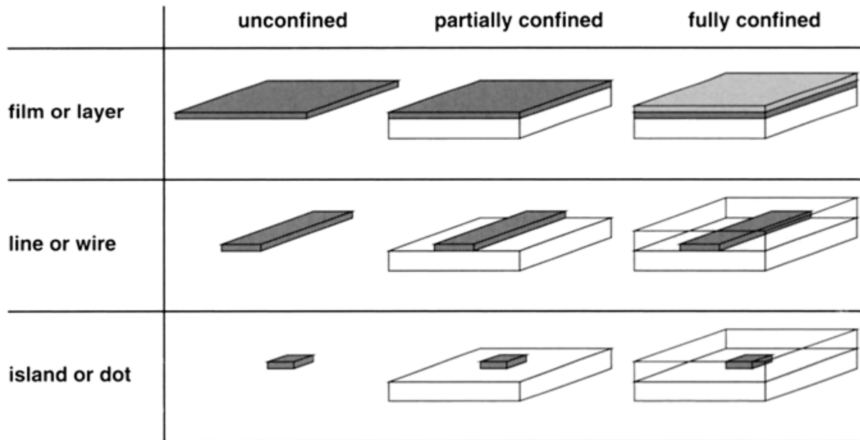

Fig. 1.1. A categorization of small volume structures in terms of their general shapes and levels of constraints. A film is often called a two-dimensional structure, a line is called a one-dimensional structure and a dot a zero-dimensional structure, but this terminology is not standard and it varies significantly among different technical specialities.

solid bodies in three orthogonal directions, with the orientation of the reference coordinate system being dictated by the configuration. The degree of constraint is determined by the interaction of the thin film structure with other deformable solids to which it may be attached or with which it may otherwise be in contact. The former situation requires compatibility of deformation, while the latter requires some restriction on its motion. The categories of configuration are termed film (or layer), line (or wire) and island (or dot); the categories of constraint are termed unconfined, partially confined and fully confined. These classes are illustrated in Figure 1.1. There is nothing fundamental about such a classification scheme, but its adoption can facilitate understanding of the ranges of applicability of the various ideas in the field.

With reference to Figure 1.1, a structure of an extent that is small in one direction compared to its extent in the other two directions is termed a thin film; in structural mechanics, such configurations are identified as plates or shells. The qualifier 'small' as used here means that the largest dimensions are at least twenty times greater than the small dimension, and more commonly are hundreds of times greater than the small dimension. A structure that has small extent in two directions compared to its extent in the third direction is termed a line or wire; such configurations are usually identified as rods or bars in structural mechanics. Lastly, a structure that has small extent in all three directions, compared to the dimensions of its surroundings in this case, is termed an island or a dot.

Concerning the degree of constraint on deformation, a small structure is said to be unconfined if the boundaries associated with its thin dimensions are free to displace

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without restriction. On the other hand, it is said to be fully confined if all boundaries associated with its thin dimensions are constrained against deformation. In virtually all cases, the constraint at a boundary is due to another material which shares that boundary as a common interface. The structure is said to be partially confined if displacement of its boundaries associated with some, but not all, directions of thinness are unconstrained.

The classification matrix in Figure 1.1 includes some illustrations of varying degrees of confinement and thinness. As a specific example, consider a layer of a SiGe alloy 1 μm in thickness, which is deposited on a 1 cm by 1 cm area of a Si substrate that is 0.5 mm thick. This configuration results in a partially confined thin film structure. A stripe of copper with a square cross-section that is 0.5 μm on a side and a length of 5 mm deposited on a relatively thick Si substrate is a partially confined line. If the surfaces of the Si substrate and the wire are then completely covered over with a 1 μm thick coating of SiO_2 to electrically isolate the wire, the structure becomes a fully confined line. An InAs quantum dot being formed by stress-driven surface diffusion is a partially confined island. If this configuration is then covered over by a blanket deposit of AlAs, the final structure is a fully confined island or quantum dot configuration.

The idea of the classification scheme is intended only as a conceptual guide. There are many situations in which the structure exhibits behavior represented by more than one entry in the categorization matrix in Figure 1.1. For example, suppose that a thin film bonded to a relatively thick substrate supports a compressive stress. This is a partially confined thin film configuration. If the stress becomes large enough in magnitude, the film will tend to buckle by debonding from the substrate over some portion of the interface and then deflecting away from the substrate over this portion. The region of the buckle becomes an unconfined film but the remainder of the film is partially confined.

The categorization of thin film systems as summarized in Figure 1.1 is based on relative physical dimensions and makes no reference to any length scale reflecting the underlying structure of the material. There is usually a heirarchy of such length scales associated with a material of given chemical composition, and the scales can depend on the processing methods used to form the material structure. For example, for a polycrystalline film, intrinsic length scales include the size of the atomic unit cell, the spacing of crystalline defects and the size of the crystal grains, at the very least. Thus, a further subcategorization of film configurations based on a comparison of the small dimension of the thin structure to the *absolute* length scale characteristic of the constituent material must be considered.

When the thickness of the film is small compared to that of the substrate (typically by a factor of 50 or more), it represents a *mechanically thin film*. In this case,

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the film material either has no intrinsic structural length scales, as in the case of an amorphous film, or the film thickness is much larger than all the characteristic microstructural length scales such as the grain size, dislocation cell size, precipitate or particle spacing, diameter of the dislocation loops, mean free path for dislocation motion, or the magnetic domain wall size. Such structures, typically tens or hundreds of micrometers in thickness, are deposited onto substrates by plasma spray or physical vapor deposition, or layers bonded to substrates through welding, diffusion bonding, explosion cladding, sintering or self-propagating high temperature combustion synthesis. This definition, of course, holds only when the size scale of the microstructure is small compared to the film thickness. The continuum mechanics approach to be presented for the analysis of stress, substrate curvature and fracture in such mechanically thin films applies to a broad range of practical situations.

When the small dimension of the material structure is comparable to the characteristic microstructural size scale, the film is considered to be a *microstructurally thin film*. Most metallic thin films used in microelectronic devices and magnetic storage media are examples of microstructurally thin films, where the film thickness is substantially greater than atomic or molecular dimensions. Although the film thickness normally includes only a few microstructural units in these cases, the plane of the film has dimensions significantly larger than the characteristic microstructural size scale. The mechanical properties of these films are much more strongly influenced by such factors as average grain size, grain shape, grain size distribution and crystallographic texture than in the case of mechanically thin films. Grain to grain variations in crystallographic orientation as well as crystalline anisotropy of thermal, electrical, magnetic and mechanical properties also have a more pronounced effect on the overall mechanical response of microstructurally thin films. The mechanisms and mechanics of microstructurally thin films are considered extensively throughout this book. A microstructurally thin film can be patterned into lines or stripes on the substrate surface, in which case the cross-sectional dimensions of each line are comparable to the microstructural unit dimension. For single crystal films epitaxially bonded to relatively thick substrates, the only microstructurally significant dimension is the lattice spacing. Consequently, such films can usually be treated as microstructurally thin films even though the film thickness may be as small as several times the atomic unit cell dimension. Such structures are studied in Chapter 6.

Atomically thin films constitute layers whose thicknesses are comparable to one or a few atomic layers. An adsorbed monolayer of gas or impurity atoms on a surface is an example of an atomically thin layer. Here the mechanical response of the thin layer is likely to be more influenced by interatomic potentials and surface energy than by macroscopic mechanical properties or by micromechanisms of deformation.

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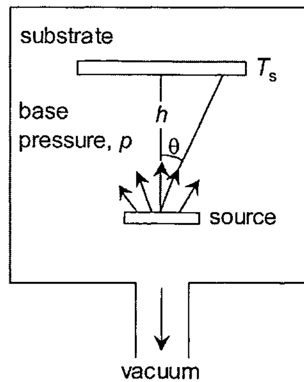

Fig. 1.2. Schematic showing the basic features of an evaporative deposition system.

1.2 Film deposition methods

Physical vapor deposition (PVD) and chemical vapor deposition (CVD) are the most common methods for transferring material atom by atom from one or more sources to the growth surface of a film being deposited onto a substrate. Vapor deposition describes any process in which a solid immersed in a vapor becomes larger in mass due to transference of material from the vapor onto the solid surface. The deposition is normally carried out in a vacuum chamber to enable control of the vapor composition. If the vapor is created by physical means without a chemical reaction, the process is classified as PVD; if the material deposited is the product of a chemical reaction, the process is classified as CVD. Many variations of these basic vapor deposition methods have been developed in efforts to balance advantages and disadvantages of various strategies based on the requirements of film purity, structural quality, the rate of growth, temperature constraints and other factors. In this section, the salient features of these processing methods are briefly described. This is of general interest because the state of stress in a film can be strongly influenced by its deposition history, as described in the later sections of this chapter.

1.2.1 Physical vapor deposition

Physical vapor deposition is a technique whereby physical processes, such as evaporation, sublimation or ionic impingement on a target, facilitate the transfer of atoms from a solid or molten source onto a substrate. Evaporation and sputtering are the two most widely used PVD methods for depositing films.

Figure 1.2 schematically illustrates the basic features of evaporative deposition. In this process, thermal energy is supplied to a source from which atoms are evaporated for deposition onto a substrate. The vapor source configuration is intended to concentrate heat near the source material and to avoid heating the surroundings.

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Heating of the source material can be accomplished by any of several methods. The simplest is resistance heating of a wire or stripe of refractory metal to which the material to be evaporated is attached. Larger volumes of source material can be heated in crucibles of refractory metals, oxides or carbon by resistance heating, high frequency induction heating or electron beam evaporation. The evaporated atoms travel through reduced background pressure p in the evaporation chamber and condense on the growth surface. The deposition rate $\dot{R}$ of the film is commonly denoted by the number of atoms arriving at the substrate per unit area of the substrate per unit time, by the time required to deposit a full atomic layer of film material, or by the average normal speed of the growth surface of the film. The deposition rate or flux is a function of the travel distance from the source to the substrate, the angle of impingement onto the substrate surface, the substrate temperature T_s and the base pressure p. If the source material (such as Cr, Fe, Mo, Si and Ti) undergoes sublimation, sufficiently large vapor pressures may be obtained below its melting temperature so that a solid source could be employed for evaporative deposition. On the other hand, for most metals in which a sufficiently large vapor pressure ($\sim 10^{-3}$ torr, or 0.13 Pa) cannot be achieved at or below the melting temperature, the source is heated to a liquid state so as to achieve proper deposition conditions.

Metal alloys, such as Al–Cu, Co–Cr or Ni–Cr, can generally be evaporated directly from a single heated source. If two constituents of the alloy evaporate at different rates causing the composition to change in the melt, two different sources held at different temperatures may be employed to ensure uniform deposition. Unlike metals and alloys, inorganic compounds evaporate in such a way that the vapor composition is usually different from that of the source. The resulting molecular structure causes the film stoichiometry to be different from that of the source. High purity films of virtually all materials can be deposited in vacuum by means of electron beam evaporation.

Molecular beam epitaxy (MBE) is an example of an evaporative method. This growth technique can provide film materials of extraordinarily good quality which are ideal for research purposes. However, the rate of growth is very low compared to other methods, which makes it of limited use for production of devices. In MBE, the deposition of a thin film can be accurately controlled at the atomic level in an ultra-high vacuum (10^{-10} torr, or 1.33×10^{-8} Pa). A substrate wafer is placed in the ultra-high vacuum chamber. It is sputtered briefly with a low energy ion beam to remove surface contamination. This step is followed by a high temperature anneal to relax any damage done to the growth surface during preparation. The substrate is then cooled to the growth temperature, typically between 400 and 700 °C, and growth commences by directing atomic beams of the film material, as well as a beam of dopant material if necessary, toward the growth surface of the substrate. The

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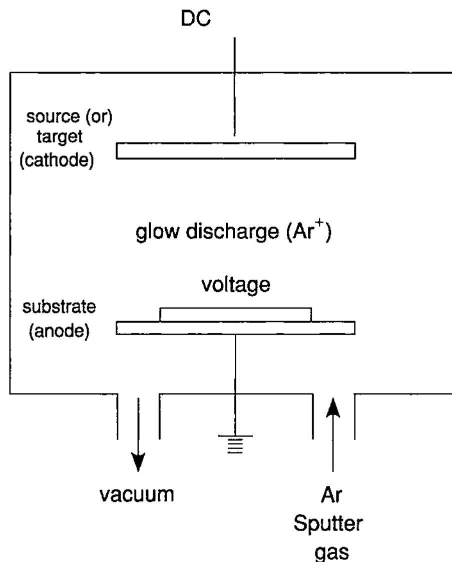

Fig. 1.3. Schematic showing the basic features of a dc sputter deposition system.

beams are emitted from crucibles of the growth materials which have been heated to temperatures well above the substrate temperature to induce evaporation and condensation. The films may be examined by transmission electron microscopy or x-ray diffraction after cooling. The complete history of evolution of internal stress in the film during deposition can be obtained *in situ* by monitoring the changes in curvature of the substrate on which the film is deposited as described in detail in Chapter 2.

In sputter deposition, ions of a sputtering gas, typically Ar, are accelerated toward the target at high speed by an imposed electric field. The initial concentration of charge carriers in the system is significantly increased with an increase in the dc voltage, as the ions collide with the cathode, thereby releasing secondary electrons, and with the neutral gas atoms. As critical numbers of electrons and ions are created through such avalanches, the gas begins to glow and the discharge becomes self-sustaining. Gaseous ions striking the target or the source material from which the film is made dislodge surface atoms which form the vapor in the chamber. The target is referred to as the cathode since it is connected to the negative side of the direct current power supply. Figure 1.3 schematically shows the basic elements of a sputter deposition system. The chamber is evacuated and then Ar gas, at a pressure of approximately 13.3 Pa (10^{-1} torr), is introduced for the purpose of maintaining a visible glow discharge. The Ar^+ ions bombard the target or cathode, and the ensuing momentum transfer causes the neutral atoms of the target source to be dislodged. These atoms transit through the discharge and condense onto the substrate, thus providing film growth.

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Several different sputtering methods are widely used for the deposition of thin films in different practical applications: (i) dc sputtering (also commonly referred to as cathodic or diode sputtering), (ii) radio frequency (rf) sputtering with frequencies typically in the 5–30 MHz range, (iii) magnetron sputtering, where a magnetic field is applied in superposition with a parallel or perpendicularly oriented electric field between the substrate and the target source, and (iv) bias sputtering, where either a negative dc or rf bias voltage is applied to the substrate so as to vary the energy and flux of the incident charged species.

There are many distinctions between the sputtering process and the evaporative process for film deposition, as described by Ohring (1992) for example. Evaporation is a thermal process where the atoms of the material to be deposited arrive at the growth surface with a low kinetic energy. In sputtering, on the other hand, the bombardment of the target source by Ar^+ ions imparts a high kinetic energy to the expelled source atoms. Although sputter deposition promotes high surface diffusivity of arriving atoms, it also leads to greater defect nucleation and damage at the deposition surface because of the high energy of the atoms. While evaporation occurs in a high vacuum (10^{-6} to 10^{-10} torr, or 1.33×10^{-4} to 1.33×10^{-8} Pa), sputtered atoms transit through a high pressure discharge zone with a pressure of approximately 0.1 torr (13.33 Pa). Sputter-deposited films generally contain a higher concentration of impurity atoms than do films deposited by evaporation and are prone to contamination by the sputtering gas. As a result, sputter deposition is not well suited for epitaxial growth of films.

For polycrystalline films, the film grain structure resulting from sputter deposition typically has many crystallographic orientations without preferred texture. However, evaporative deposition leads to highly textured films for which the grain size is typically greater than that of the sputtered films. Sputter deposition offers better control in maintaining stoichiometry and film thickness uniformity than evaporative deposition and has the flexibility to deposit essentially any crystalline and amorphous materials. These issues are discussed in more detail in Section 1.8.

1.2.2 Chemical vapor deposition

Chemical vapor deposition is a versatile deposition technique that provides a means of growing thin films of elemental and compound semiconductors, metal alloys and amorphous or crystalline compounds of different stoichiometry. The basic principle underlying this method is a chemical reaction between a volatile compound of the material from which the film is to be made with other suitable gases so as to facilitate the atomic deposition of a nonvolatile solid film on a substrate, as indicated schematically in Figure 1.4. The chemical reaction in a CVD process may involve pyrolysis or reduction.

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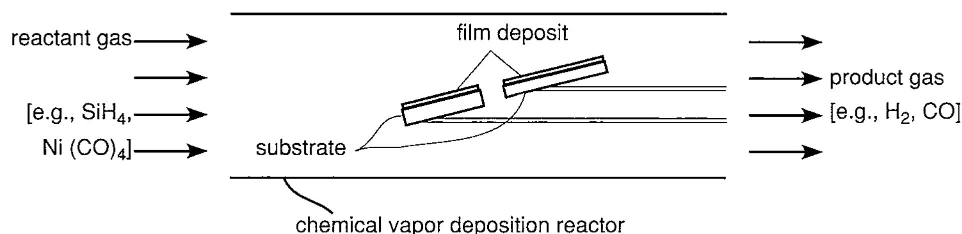
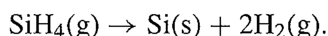


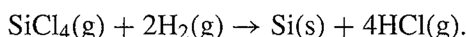
Fig. 1.4. Schematic showing the basic features of an open reactor system for chemical vapor deposition.

Consider the production of amorphous or polycrystalline Si films on Si substrates, where pyrolysis at 650 °C leads to the decomposition of silane gas according to the reaction



$$SiH_4(g) \rightarrow Si(s) + 2H_2(g).$$

High-temperature reduction reactions where hydrogen gas is used as a reducing agent are also employed to produce epitaxial growth of Si films on monocrystalline Si substrates at 1200 °C according to the reaction



$$SiCl_4(g) + 2H_2(g) \rightarrow Si(s) + 4HCl(g).$$

The nature of epitaxy is described in detail later in this chapter.

In CVD, as in PVD, vapor supersaturation affects the nucleation rate of the film whereas substrate temperature influences the rate of film growth. These two factors together influence the extent of epitaxy, grain size, grain shape and texture. Low gas supersaturation and high substrate temperatures promote the growth of single crystal films on substrates. High gas supersaturation and low substrate temperatures result in the growth of less coherent, and possibly amorphous, films. Low-pressure CVD (LPCVD), plasma-enhanced CVD (PECVD), laser-enhanced CVD (LECVD) and metal-organic CVD (MOCVD) are variants of the CVD process used in many situations to achieve particular objectives.

1.2.3 Thermal spray deposition

The thermal spray process of thin film fabrication refers broadly to a range of deposition conditions wherein a stream of molten particles impinges onto a growth surface. In this process, which is illustrated schematically in Figure 1.5, a thermal plasma arc or a combustion flame is used to melt and accelerate particles of metals, ceramics, polymers or their composites to high velocities in a directed stream

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