

Thin Films and Vapor Deposition

CHAPTER SUMMARY

Thin films are often deposited relatively slowly so that the growth can be strongly influenced by the substrate, which plays a key role in determining film microstructure and properties. The substrate is much more important in growing thin films than it is for thick films and is a crucial factor if we want to grow oriented (epitactic) films. At the end of this chapter we describe some of the requirements for the substrate. The growth techniques described in this chapter involve vacuum chambers and are generally expensive so that thick films are grown by other methods, particularly when epitaxy is not required. Much of this topic is carried over from the semiconductor industry and is often not thought of as ceramic processing. However, without thin films of Si oxide and Si nitride, “Silicon Valley” might still be green fields.

28.1 THE DIFFERENCE BETWEEN THIN FILMS AND THICK FILMS

In Chapter 27 we described how thick films of ceramics are produced. The difference between thick films and thin films is not really the thickness of the layer; it is how the layer is formed. In general, thin films are ≤ 500 nm in thickness whereas thick films may be several tens of micrometers in thickness or even thicker depending upon the particular application. Thin films are generally prepared from the vapor phase whereas for thick films we use a solution or slurry. Furthermore, thin films are often crystallographically oriented in a particular way with respect to the underlying substrate. This orientation relationship, known as epitaxy, is determined by the crystal structures and lattice parameters of the film and the substrate. In general, thick films and coatings have no specific orientation and contain a large number of randomly oriented crystalline grains.

28.2 ACRONYMS, ADJECTIVES, AND HYPHENS

The thinnest thin films are almost exclusively formed from the vapor or gaseous phase and although there are many different deposition techniques they can be divided into two basic classes:

- Physical vapor deposition (PVD)
- Chemical vapor deposition (CVD)

Chemical vapor deposition techniques use either gas phase reactions or gaseous decomposition as the source of material. Physical vapor deposition techniques rely on excitation of a source (sometimes called the target) that is usually solid to produce the necessary material for film formation. In addition to the basic difference in the way that material transfer from the vapor phase to the solid phase is accomplished, there are other differences between CVD and PVD. For example, CVD is often used to produce thicker films (i.e., films >1 μm in thickness). The reason is that the growth rate by CVD is on the order of micrometers per minute (e.g., 2 $\mu\text{m}/\text{min}$), whereas for PVD techniques the growth rate is often orders of magnitude lower (e.g., growth rates in the range 0.01 – 0.03 $\mu\text{m}/\text{min}$ are typical). There are other differences that will become evident as we describe the different techniques in the following sections.

Thin-film technology is replete with acronyms and several of the main ones you will encounter are listed in Table 28.1. Molecular beam epitaxy (MBE) is the only acronym that assumes a crystalline structure and alignment of the thin film. Molecular-beam evaporation would be much better, especially when used to grow amorphous films!

We defined epitaxy in Chapter 15. Incidentally, the grammatically correct adjective from epitaxy is epitactic or better still epitaxial, but epitaxial has come to be accepted even by the *Oxford English Dictionary* because it is now so widely used. In many of the deposition techniques, it is not clear where the hyphen(s) should be (if there should be one) but thin-film growth is always the way to grow thin films and adverbs are never hyphenated to parts of verbs.

TABLE 28.1 Some Common Acronyms in Thin-Film Technology

<i>CVD technique</i>	<i>Chemical vapor deposition</i>	<i>PVD technique</i>	<i>Physical vapor deposition</i>
APCVD	Atmospheric-pressure CVD	MBE	Molecular-beam epitaxy
LECVD	Laser-enhanced CVD	PLD	Pulsed-laser deposition
LPCVD	Low-pressure CVD	IBAD	Ion-beam-assisted deposition
MOCVD	Metal-organic CVD	RE	Reactive evaporation
PECVD	Plasma-enhanced CVD		

28.3 REQUIREMENTS FOR THIN CERAMIC FILMS

There are four general characteristics that we usually want to control when growing ceramic thin films:

- Crystal structure
- Stoichiometry
- Phase
- Surface morphology/topography

We will now look at each of these characteristics and explain the rationale behind why they are important. The thin film may be crystalline, often epitaxial, or sometimes polycrystalline or amorphous. The reason for requiring crystallinity is that for thin films we are often making use of a particular electronic, optical, or magnetic property of the material. These properties are frequently anisotropic. Hence we want to ensure that the film is crystalline and oriented in the correct way to optimize the desired property. This alignment is best achieved by judicious choice of substrate and, therefore, we make use of epitaxy. Many properties of ceramic thin films are affected by the presence of grain boundaries. In epitaxial films it is often possible to control the types of grain boundary that are produced. Generally these boundaries are low-angle grain boundaries, but they can be high-angle grain boundaries that may be associated with large distortions.

The correct stoichiometry, or composition, is necessary because for some materials they exhibit the required property only within a certain composition range. An example is the high-temperature superconductors whose structures we described in Chapter 7. For $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ (YBCO), the value of the superconducting transition temperature depends on the value of x . When x is close to one the transition temperature is ~ 90 K. When $x = 0.3$ the transition temperature is reduced to 30 K. The change in oxygen stoichiometry is associated with a change in the structure of the material. Many technologically important ceramics exist in different crystalline forms. Another

example is BaTiO_3 . The ferroelectric form of BaTiO_3 is tetragonal.

The final characteristic is the film surface. In general we want to have smooth films, but this requirement is not universal and is really based on what we want to do with the film. If the film is part of a multilayer structure, i.e., there are going to be other layers deposited on top, then it is clearly important for the underlying surface to be smooth. If the film is to be patterned using photolithographic techniques (the same techniques used to pattern semiconductor devices) then smooth surfaces are essential. Some properties are dependent upon surface roughness. For example, rough surfaces can contribute strongly to propagation losses in films used for guiding microwave radiation.

From the above discussion you can see that there are several stringent requirements for ceramic thin films. For this reason, there are numerous techniques that have been used to form such films. Some techniques work better for some materials whereas other techniques work better for other materials. We describe some of the techniques used to form ceramic thin films in the following sections, but this is not a comprehensive list.

28.4 CHEMICAL VAPOR DEPOSITION

Chemical vapor deposition involves either

- Chemically reacting a volatile compound of a material to be deposited, with other gases, to produce a non-volatile solid or
- Pyrolysis (decomposition) of a compound at high temperature to produce a solid.

In either case the solid forms as a film on a suitably placed substrate. It is important that the reaction takes place only on the substrate surface. If the reaction takes place in the gas stream above the substrate then particulates will form. Under these conditions the film will have a low density and a large number of voids. There are several different geometries for a CVD reactor and some of these are illustrated in Figure 28.1. The substrates are usually placed on a graphite slab, which acts as a susceptor for radiofrequency induction heating. The gases are introduced into the reactor chamber, sometimes in the presence of an inert carrier gas such as argon. As an example of a CVD reaction consider the formation of SiC from silicon tetrachloride (SiCl_4) and methane (CH_4):



Silicon tetrachloride is a liquid at room temperature and can easily be vaporized (it boils at 57.6°C) and transported to the reactor chamber. Methane can be supplied as a high-purity gas directly from a bottle. The reaction between SiCl_4 and CH_4 to produce SiC films occurs at 1400°C . Two aspects of the temperature are important:

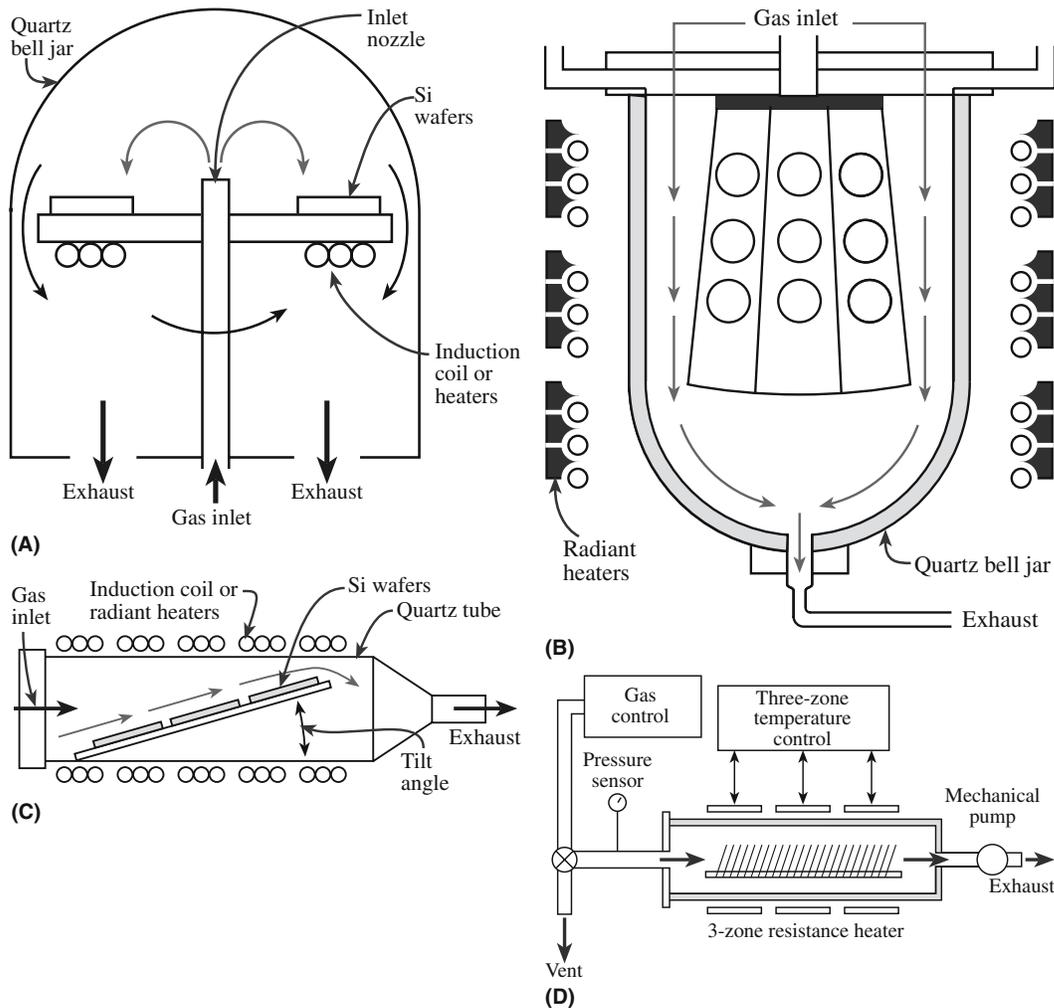
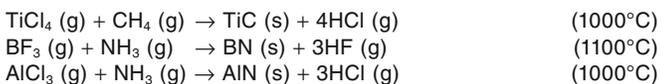


FIGURE 28.1 Examples of CVD reactor configurations: (a) pancake, (b) barrel, (c) horizontal, (d) LPCVD.

- It must be sufficiently high so that the reaction occurs.
- If an epitactic deposit is required, it must be high enough to allow the condensing species to diffuse across the crystal surface to find their required lattice crystal positions.

A variety of oxide, carbide, nitride, and boride films and coatings can be readily prepared by CVD techniques as shown in Table 28.2. The reacting compounds must exist in a volatile form and must be sufficiently reactive in the gas phase. Examples of other reactions that can be used to produce ceramic films by CVD are given below:



ELECTRONIC GRADE SILICON (EGS)

The annual worldwide production capacity is $>10^7$ kg. It is all made by CVD.

Chemical vapor deposition is one of the most important deposition techniques for forming ceramic films and coatings. We described two examples in Chapter 20 in which CVD is used in composites. It is used to form SiC fibers by the reaction between CH_3SiCl_3 and H_2 on a tungsten wire. It is also used to form the matrix phase in a ceramic matrix composite (CMC) by a process known as chemical-vapor infiltration. In later chapters we describe the CVD technique again, e.g., it is used in the formation of optical fibers.

Before we leave this section there is one additional example of the importance of CVD. All of the electronic grade silicon (EGS) used in the fabrication of silicon wafers is made by CVD. The highest purity EGS is made by decomposition of silane (SiH_4), which itself can be prepared in extremely high purity. The substrate is an electrically heated U-shaped rod made of single crystal silicon. The silane decomposes to form silicon, which deposits on the U-shaped rod in the form of

TABLE 28.2 Examples of Ceramic Films and Coatings Produced by CVD				
Film	Substrate	Reactants	Deposition T (°C)	Crystallinity ^a
Si	Si	Either SiCl ₂ H ₂ , SiCl ₃ H, or SiCl ₄ + H ₂ SiH ₄ + H ₂	1050–1200 600–700	E P
Ge	Ge	GeCl ₄ or GeH ₄ + H ₂	600–900	E
SiC	Si	SiCl ₄ , toluene, H ₂	1100	P
AlN	Sapphire	AlCl ₃ , NH ₃ , H ₂	1000	E
In ₂ O ₃ :Sn	Glass	In-chelate, (C ₄ H ₉) ₂ Sn(OOCH ₃) ₂ , H ₂ O	500	A
ZnS	GaAs, GaP	Zn, H ₂ S, H ₂	825	E
CdS	GaAs, sapphire	Cd, H ₂ S, H ₂	690	A
Al ₂ O ₃	Si	Al(CH ₃) ₃ + O ₂	275–475	A
	Cemented carbide	AlCl ₃ , CO ₂ , H ₂	850–1100	A
SiO ₂	Si	SiH ₄ + O ₂	450	A
		SiCl ₂ H ₂ + 2N ₂ O	900	
Si ₃ N ₄	SiO ₂	SiCl ₂ H ₂ + NH ₃	~750	A
SiNH	SiO ₂	SiH ₄ + NH ₃ (plasma)	300	A
TiO ₂	Quartz	Ti(OC ₂ H ₅) ₄ + O ₂	450	A
TiC	Steel	TiCl ₄ , CH ₄ , H ₂	1000	P
TiN	Steel	TiCl ₄ , N ₂ , H ₂	1000	P
BN	Steel	BCl ₃ , NH ₃ , H ₂	1000	P
TiB ₂	Steel	TiCl ₄ , BCl ₃ , H ₂	>800	P

^aE, epitaxial; P, polycrystalline; A, amorphous.

a columnar “feather-like” polycrystalline layer as shown in Figure 28.2. The overall thickness of this layer can exceed 5 cm, so CVD can be used to produce very “thick” films!

28.5 THERMODYNAMICS OF CHEMICAL VAPOR DEPOSITION

Thermodynamics indicates whether a particular chemical reaction is feasible. However, it will not provide any information about the speed of the reaction and film growth rates. Even if a reaction is thermodynamically possible, if

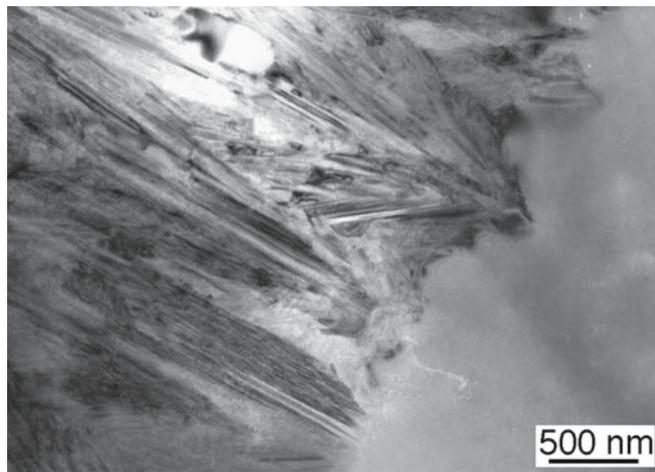


FIGURE 28.2 TEM image showing a polysilicon layer grown on a single crystal Si rod by CVD.

it proceeds at very low rates then it will not be commercially useful.

We can calculate the standard free energy, ΔG^0 , of many reactions using tabulations of thermodynamic data. Consider the reaction between TiCl₄ and CH₄:



To find the standard free energy, ΔG_r^0 , for this reaction we need to consider the standard free energies for forming the reactants and the products from their elements in the standard state at the temperature of interest. If we assume a reaction temperature of 1200 K we can look up ΔG^0 for the individual reactions below:

Ti + 2Cl ₂	→ TiCl ₄	$\Delta G_1^0 = -610 \text{ kJ}$
C + 2H ₂	→ CH ₄	$\Delta G_2^0 = 42 \text{ kJ}$
1/2H ₂ + 1/2Cl ₂	→ HCl	$\Delta G_3^0 = -102 \text{ kJ}$
Ti + C	→ TiC	$\Delta G_4^0 = -171 \text{ kJ}$

From basic thermodynamics we know

$$\Delta G_r^0 = \sum \Delta G^0 \text{ products} - \sum \Delta G^0 \text{ reactants} \quad (28.3)$$

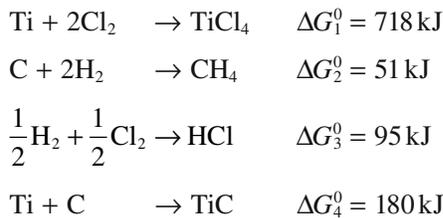
Hence, for the reaction in Eq. 28.2

$$\Delta G_r^0 = (\Delta G_4^0 + \Delta G_3^0) - (\Delta G_2^0 + \Delta G_1^0) \quad (28.4)$$

The numbers are

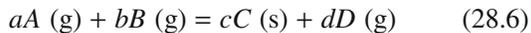
$$\Delta G_r^0 = [-171 + 4(-102)] - (42 - 610) = -11 \text{ kJ} \quad (28.5)$$

The negative value of ΔG_r^0 indicates that the reaction will proceed spontaneously at 1200 K to produce TiC. Consider a similar calculation at 298 K instead of 1200 K. The calculated values for ΔG^0 are now



Therefore, at a temperature of 298 K the value of ΔG_r^0 is +109 kJ. The positive value of ΔG_r^0 indicates that the reaction between TiCl_4 and CH_4 to form TiC will not proceed spontaneously at room temperature.

We now consider a generalized chemical reaction between two gases *A* and *B* to produce a solid *C* and another gas *D*.



The equilibrium constant for this reaction is

$$K = [C]^c [D]^d / [A]^a [B]^b \quad (28.7)$$

where [] indicates the equilibrium activity of each component of the reaction. As usual, we can take the activity of a pure stable component as unity. Pressures may be used to approximate the activities of the gaseous species, hence

$$K \approx (pD)^d / (pA)^a (pB)^b \quad (28.8)$$

where (*p*) are the equilibrium pressures of the reactants and products. The driving force for growth may be expressed as

$$\Delta G_r^0 = -RT \ln K \quad (28.9)$$

R, the gas constant, is $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$.

It is usually desired that the concentration of the volatile reactant species be fairly high so that the transport of reactants to the substrate is very rapid. If the concentration of reactants is too low, it will be difficult to produce a reasonable flow of material to the substrate surface. Thus, we want the value of *K* to be small. Assuming that the reaction to produce TiC was carried out in a closed system (so that the HCl was not being removed), the value of $\ln K$ would be 1.1. [Sometimes the equilibrium constant term is expressed as a logarithm in base 10 (log) rather than as a natural logarithm, ln; the desired value would then be $\log K = 0.5$.] When $\ln K$ is very large, the driving force is very large, which tends to produce a polycrystalline film rather than

CVD
This is an empirical method of film growth guided by thermodynamics.

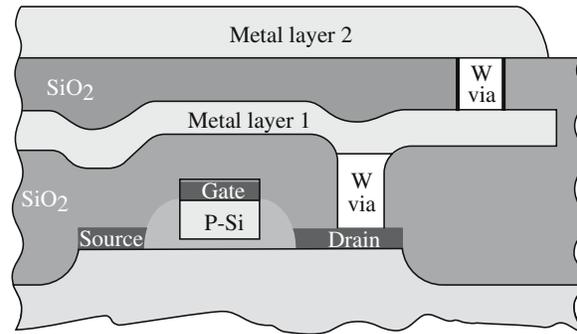


FIGURE 28.3 Schematic cross section of a multilayer metallization to a polysilicon gate field effect transistor. The contacts to the source and drain are silicides. Tungsten is used to provide vertical interconnects through vias in the oxide layer.

single-crystal epitaxial films. The use of thermodynamics implies that chemical equilibrium has been attained. Although this may occur in a closed system, it is generally not the case in an open system such as a flow reactor, where gaseous reactants and products are continuously introduced and removed.

28.6 CHEMICAL VAPOR DEPOSITION OF CERAMIC FILMS FOR SEMICONDUCTOR DEVICES

Ceramic films are widely used in the fabrication of semiconductor devices. The two materials that are presently of major interest are silicon dioxide (SiO_2) and silicon nitride (Si_3N_4). These are deposited as thin films using CVD.

SiO_2 films can be deposited with, or without, dopants. Undoped it has multiple uses:

- Insulating layer between multilevel metallizations (Figure 28.3)
- Implantation or diffusion mask
- Capping layer over doped regions to prevent outdiffusion during thermal cycling

A suitable reaction to produce SiO_2 is the oxidation of silane (SiH_4) at 450°C :



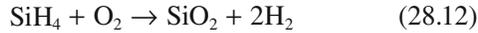
Above 600°C water vapor is produced:



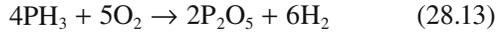
The SiO_2 film produced by either of the above two reactions is amorphous.

For some applications we need doped SiO_2 films. Dopant species include boron and phosphorus. Doped oxide films are made by introducing dopant compounds such as phosphine (PH_3)

or diborane (B₂H₆) into the gas stream along with SiH₄ and an oxygen source. The chemical reactions for phosphorus-doped oxides are



and



Phosphorus-doped silica films are used as

- Insulators between metal layers
- Device passivation
- Diffusion sources

One application that we will describe in a little more detail is the use of phosphorus-doped glass (called P-glass in the semiconductor industry) as an insulator between polysilicon gates and the top metallization in a metal oxide semiconductor field effect transistor (MOSFET). The P-glass is used because steps formed by the polysilicon gate make uniform deposition of the metal film impossible. The P-glass layer is deposited by CVD and then heated until it softens and flows: this process is called reflow. The reflow characteristics depend on the concentration of P in the glass, which is typically between 6 and 8 wt%. Silica doped with both P and B is also used for the reflow process. Typical concentrations are 1–4 wt% B and 4–6 wt% P. The borophosphosilicate glass (BPSG) has the advantage of lower flow temperatures; however, care must be taken to carefully control the dopant concentrations, otherwise separation of a B-rich phase can occur.

Si₃N₄ layers deposited by CVD are important in the fabrication of certain semiconductor devices. One area is in the so-called LOCOS (local oxidation of silicon) process. This method is used in both bipolar and metal oxide semiconductor (MOS) devices to isolate active device regions. The process works as follows: A layer of Si₃N₄ is deposited on the silicon wafer by CVD either by reacting silane and ammonia at temperatures between 700 and 900°C



or by reacting dichlorosilane and ammonia between 700 and 800°C



Like the SiO₂ films described earlier the Si₃N₄ is amorphous. The exposed regions of the silicon wafer are then oxidized whereas the areas covered by Si₃N₄ are protected. The oxidizing agent cannot diffuse through the Si₃N₄ layer to reach the silicon surface. However, oxidation does occur a small distance below the edges of the silicon nitride layer. If the oxide layer is sufficiently thick, the edges of

the nitride film are pushed up and away from the silicon surface. After oxidation the Si₃N₄ layer is removed.

Si₃N₄ layers are also used for passivating Si devices because they act as an extremely good barrier to the diffusion of water and Na. These impurities can cause device metallization to corrode or devices to become unstable.

28.7 TYPES OF CHEMICAL VAPOR DEPOSITION

There are several forms of CVD and each form has its own acronym. If the process takes place at atmospheric pressure (AP) it is referred to simply as CVD or APCVD. In APCVD systems the gas flow is almost exclusively parallel to the surface. The reactor configurations shown in Figure 28.1 are all examples of configurations used for APCVD.

When lower pressures are used the operation is low-pressure CVD (LPCVD). The gas pressure is usually in the range 0.5–1 torr for LPCVD reactors, distinguishing it from APCVD systems operating at 760 torr. In LPCVD reactors the substrates are mounted vertically.

If a plasma is used to generate ions or radicals that recombine to give the desired film, the process is plasma-enhanced CVD (PECVD). In PECVD it is possible to use much lower substrate temperatures because the plasma provides energy for the reaction to proceed. A major commercial application of PECVD is the formation of silicon nitride films for passivation and encapsulation of semiconductor devices. At this stage of the fabrication process the device cannot tolerate temperatures much above 300°C. High temperatures would still be required if crystalline or epitaxial films were required. Many nitrides have been prepared in thin-film form by PECVD, including AlN, GaN, TiN, and BN. A more complete list of films deposited by PECVD is given in Table 28.3.

PECVD has also been used to fabricate carbon nanotubes and other one-dimensional nanostructures such as boron carbide nanowires and nanosprings. A convenient precursor for boron carbide nanowires is orthocarborane (C₂B₁₀H₁₂).

MOCVD is distinguished from other forms of CVD in that the precursors are metalorganic compounds. MOCVD is widely used in the semiconductor industry but not so widely used in forming ceramic films. One example of a ceramic film formed by MOCVD is AlN, where the precursors are trimethyl aluminum [TMAI = Al(CH₃)₃] and ammonia (NH₃)



LECVD (laser-enhanced CVD) uses a laser beam to enhance reactions at the substrate surface. One feature of this technique is that it is possible to “write” materials on the substrate: the deposit is formed only where the scanned light beam hits the substrate.

TABLE 28.3 PECVD Reactants, Deposition Temperatures, and Growth Rates

<i>Film</i>	<i>T (K)</i>	<i>Rate (cm/s)</i>	<i>Reactants</i>
a-Si	573	10 ⁻⁸ -10 ⁻⁷	SiH ₄ ; SiF ₄ -H ₂ ; Si-H ₂
c-Si	673	10 ⁻⁸ -10 ⁻⁷	SiH ₄ -H ₂ ; SiF ₄ -H ₂ ; Si-H ₂
C (graphite)	1073-1273	10 ⁻⁵	C-H ₂ ; C-N ₂
CdS	373-573	10 ⁻⁶	Cd-H ₂ S
SiO ₂	523	10 ⁻⁸ -10 ⁻⁶	Si(OC ₂ H ₅) ₄ ; SiH ₄ -O ₂ , N ₂ O
GeO ₂	523	10 ⁻⁸ -10 ⁻⁶	Ge(OC ₂ H ₅) ₄ ; GeH ₄ -O ₂ , N ₂ O
SiO ₂ /GeO ₂	1273	3 × 10 ⁻⁴	SiCl ₄ -GeCl ₄ + O ₂
Al ₂ O ₃	523-773	10 ⁻⁸ -10 ⁻⁷	AlCl ₃ -O ₂
TiO ₂	473-673	10 ⁻⁸	TiCl ₄ -O ₂
B ₂ O ₃			B(OC ₂ H ₅) ₃ -O ₂
Si ₃ N ₄ (H)	573-773	10 ⁻⁸ -10 ⁻⁷	SiH ₄ -N ₂ , NH ₃
AlN	1273	10 ⁻⁶	SiCl ₄ -N ₂
GaN	873	10 ⁻⁸ -10 ⁻⁷	GaCl ₃ -N ₂
TiN	523-1273	10 ⁻⁸ -5 × 10 ⁻⁶	TiCl ₄ -H ₂ + N ₂
BN	673-973		B ₂ H ₆ -NH ₃
SiC	473-773	10 ⁻⁸	SiH ₄ -C _n H _m
TiC	673-873	5 × 10 ⁻⁸ -10 ⁻⁶	TiCl ₄ -CH ₄ + H ₂
B _x C	673	10 ⁻⁸ -10 ⁻⁷	B ₂ H ₆ -CH ₄

28.8 CHEMICAL VAPOR DEPOSITION SAFETY

Safety issues are particularly important for CVD since many of the source compounds are toxic and disposal of waste products, e.g., HCl, is often problematic. Additional problems can occur if the reactants are pyrophoric (ignite in contact with air). Table 28.4 lists some of the source gases used in CVD and their potential hazards. Silane is widely used in the semiconductor industry and was the cause of a major explosion and fire at a manufacturing plant in Moses Lake, WA. The incident caused a number

of critical injuries and resulted in the plant being closed for several months.

28.9 EVAPORATION

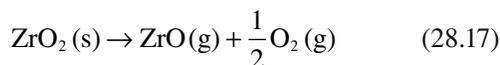
Experimentally, evaporation is a very simple method for forming thin films. The source is either a liquid or a solid that is heated to produce a flux of atoms or molecules. In general, it will be necessary to melt the material if the vapor pressure is <10⁻³ torr at its melting temperature. Most metals fall into this category and so liquid sources

TABLE 28.4 Hazardous Gases Used in CVD

<i>Gas</i>	<i>Corrosive</i>	<i>Flammable</i>	<i>Pyrophoric</i>	<i>Toxic</i>	<i>Bodily hazard</i>
Ammonia (NH ₃)	X			X	Eye and respiratory irritation
Arsine (AsH ₃)		X		X	Anemia, kidney damage, death
Boron trichloride (BCl ₃)	X				
Boron trifluoride (BF ₃)	X				
Chlorine (Cl ₂)	X			X	Eye and respiratory irritation
Diborane (B ₂ H ₆)		X	X	X	Respiratory irritation
Dichlorosilane (SiH ₂ Cl ₂)	X	X			
Germane (GeH ₄)		X		X	
Hydrogen chloride (HCl)	X				
Hydrogen fluoride (HF)	X				Severe burns
Hydrogen (H ₂)		X			
Phosphine (PH ₃)		X	X	X	Respiratory irritation, death
Phosphorus pentachloride (PCl ₅)	X				
Silane (SiH ₄)		X	X	X	
Silicon tetrachloride (SiCl ₄)	X				

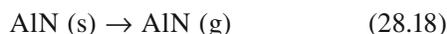
are used. Some metals reach sufficiently high vapor pressures below their melting temperature (e.g., Cr) and can be used as solids.

Evaporation of metals is generally straightforward because they evaporate either as atoms or as clusters of atoms. However, most compounds dissociate when heated and therefore the vapor composition will be different from that of the source. Consequently, the stoichiometry of the deposited film will also be different from that of the source. An example of an oxide that dissociates on heating is ZrO_2



Films formed directly from evaporation of ZrO_2 tend to be metal rich. To maintain the desired stoichiometry it is necessary to perform the evaporation in an oxygen-rich environment. This is called reactive evaporation (RE). A similar approach needs to be used with SiO_2 , GeO_2 , TiO_2 , and SnO_2 .

Some ceramics sublime, i.e., they go from a solid to a vapor without dissociation, for example



Thus film stoichiometry would be maintained in the deposit. Several oxides also behave in this way, for example, B_2O_3 , GeO , and SnO .

For some ceramics the high sublimation temperatures require special heating sources for evaporation. One such source is a focused electron beam. The process is then called electron beam (or simply e-beam) evaporation.

28.10 SPUTTERING

An example of a simple sputtering system is shown in Figure 28.4. Atoms are dislodged from a solid target through the impact of energetic gaseous ions. The usual sputtering gas is argon, which is ionized forming a plasma. An argon plasma has a characteristic purple color, which you see during sputter coating of samples for scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analysis. The plasma forms as a result of collisions between energetic electrons in the gas and the argon atoms. The positive Ar^+ ions in the plasma are attracted toward the cathode (the *target*) and the electrons toward the anode (the *substrate*). The energy of the Ar^+ depends on the value of the applied electric field, but is sufficient to cause atoms to be ejected from the target surface. When an ion reaches the target it collects an electron, supplied via the external circuit from the anode, and become a neutral atom that returns to the gas to be reionized. A

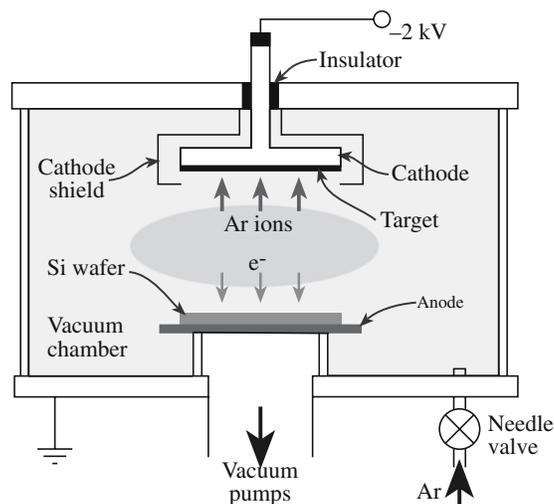


FIGURE 28.4 Schematic of a sputtering system.

substrate placed facing the cathode will be coated with a film of the material sputtered off the target surface. [If you have any experience with sputter coating samples for electron microscopy you will realize that the inside walls of the vacuum chamber also become coated.] A wide range of ceramics can be deposited by sputtering; some examples are given in Table 28.5.

There are several characteristics of the sputtering process that need to be considered before using this technique for film growth:

- It does not involve melting and therefore materials with high melting points can be deposited.
- It is a relatively slow process.
- It may be difficult to maintain stoichiometry of a multicomponent target due to the different sputtering rates of the constituents.
- When the substrate and target are facing each other (on-axis configuration) the growing film may be damaged by bombardment by energetic species from the plasma.

As with CVD and evaporation, there are various types of sputtering. The process we have described so far is DC sputtering, also called diode or cathodic sputtering. It is the easiest process to visualize, but cannot be used for insulating targets. There are two approaches for ceramics:

- Reactive sputtering uses DC sputtering of a metal target in a reactive gas environment. For example, we can make AlN films by sputtering an Al target in either nitrogen or ammonia (mixed in with the working gas, Ar).
- RF sputtering uses an alternating RF signal between the electrodes. Typical frequencies are between 5 and 30 MHz.

Ar IN PLASMA FORMATION

It is used because of its high mass, which creates a high momentum and more ejected particles from the target.

TABLE 28.5 Ceramic Sputtering Targets

<i>Material</i>	<i>Applications</i>
<i>Oxides</i>	
Al ₂ O ₃	Insulation, protective films for mirrors
BaTiO ₃ , PbTiO ₃	Thin-film capacitors
CeO ₂	Antireflection coatings
In ₂ O ₃ -SnO ₂	Transparent conductors
LiNbO ₃	Piezoelectric films
SiO ₂	Insulation
SiO	Protective films for mirrors, infrared filters
Ta ₂ O ₅ , TiO ₂ , ZrO ₂ , HfO ₂ , MgO	Dielectric films for multilayer optical coatings
Yttrium aluminum garnet (YAG), yttrium iron garnet (YIG), gadolinium gallium garnet (GGG, Gd ₃ Ga ₅ O ₁₂)	Magnetic bubble memory devices
YVO ₃ -Eu ₂ O ₃	Phosphorescent coating on special currency papers
YBa ₂ Cu ₃ O ₇	High-temperature superconductors
<i>Fluorides</i>	
CaF ₂ , CeF ₃ , MgF ₂ , ThF ₄ , Na ₃ AlF ₆ (cryolite)	Dielectric films for multilayer optical coatings (antireflection coatings, filters, etc.)
<i>Borides</i>	
TiB ₂ , ZrB ₂	Hard, wear-resistant coatings
LaB ₆	Thermionic emitters
<i>Carbides</i>	
SiC	High-temperature semiconduction
TiC, TaC, WC	Hard, wear-resistant coatings
<i>Nitrides</i>	
Si ₃ N ₄	Insulation, diffusion barriers
TaN	Thin-film resistors
TiN	Hard coatings
<i>Silicides</i>	
MoSi ₂ , TaSi ₂ , TiSi ₂ , WSi ₂	Contacts, diffusion barriers in integrated circuits
<i>Sulfides</i>	
CdS	Photoconductive films
MoS ₂ , TaS ₂	Lubricant films for bearings and moving parts
ZnS	Multilayer optical coatings
<i>Selenides, tellurides</i>	
CdSe, PbSe, CdTe	Photoconductive films
ZnSe, PbTe	Optical coatings
MoTe, MoSe	Lubricants

28.11 MOLECULAR-BEAM EPITAXY

Molecular-beam epitaxy is a technique that has mainly been used by the semiconductor industry for producing thin films of compound semiconductors (e.g., GaAs and InP) used in the fabrication of LEDs, laser diodes, etc. Because these inorganic semiconductors are ceramics it should not be surprising that the technique can also be used to grow other ceramic thin films, such as the high-temperature superconductor YBa₂Cu₃O₇. In fact, MBE is ideal for ceramics that have layered structures because it allows precise sequential deposition of single monolayers.

A diagram of an MBE system is shown in Figure 28.5. The materials to be deposited are usually evaporated from

separate furnaces called Knudsen effusion cells, which are bottle-shaped crucibles with a narrow neck. A resistance heater wound around the cell provides the heat necessary to evaporate the material. As in the case of conventional evaporation the source may be solid or liquid depending upon its vapor pressure. The rate of deposition of each species is determined by the vapor pressure above the source, which is a strong function of temperature. The temperature of each of the Knudsen effusion cells therefore controls the flux of atoms reaching the substrate.

Molecular-beam epitaxy of semiconductors requires the use of an ultrahigh vacuum (UHV) chamber (background pressure 10⁻⁸-10⁻¹⁰ torr). For oxide ceramics background pressures of ≤10⁻⁴ torr are more common. The high vacuum requirement of MBE presents a problem for the growth of

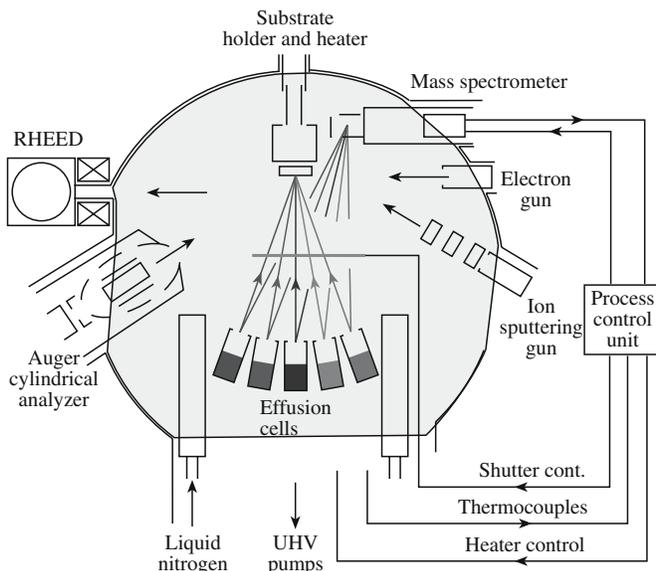


FIGURE 28.5 Schematic of an MBE system.

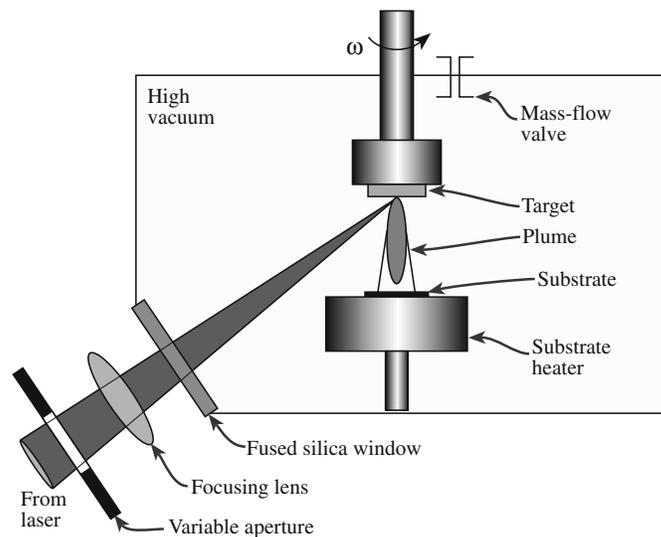


FIGURE 28.6 Schematic of a PLD system.

many multicomponent oxides such as the high-temperature superconductors because most of these compounds require oxygen pressures much higher than this to form. This limitation has been overcome by the use of highly oxidizing gases, such as NO_2 , atomic O, or O_3 , near the surface of the growing film, while the background pressure is maintained as low as possible.

In addition to the requirement of high vacuum or UHV environments, other features of MBE limit its use:

- The equipment is expensive (>\$1 million) so the value added must be high.
- Deposition rates are low: $\leq 1 \mu\text{m/h}$ is typical.

28.12 PULSED-LASER DEPOSITION

In pulsed-laser deposition (PLD) a laser beam is used to ablate material from a solid target. The experimental arrangement, which is very simple, is shown in Figure 28.6. However, the laser–target interactions are very complex and result in the formation of a plume of material (often visible and brightly colored) that contains all the necessary components (often in the correct proportions) for film growth.

PRESSURE

Pressure is often quoted in the non-SI units of torr, 1 torr being equivalent to 1 mmHg. The SI unit for pressure is the pascal, Pa. One Pa is equal to one newton per square meter (N/m^2). To convert between torr and Pa, simply multiply the pressure in torr by 133.3 to obtain the pressure in Pa ($750 \text{ torr} = 10^5 \text{ Pa}$).

PLD GROWTH OF BaTiO_3 THIN FILMS CONDITIONS

Chamber evacuated to $<5 \mu\text{torr}$
 Pressure during deposition 400 mtorr of O_2
 KrF excimer laser $\lambda = 248 \text{ nm}$
 Pulse repetition rate 50 Hz
 Pulse energy 85 mJ
 Target to substrate distance 4 cm
 Substrate temperature 750°C

Excimer lasers operating in the UV are the laser of choice for most PLD systems. The operating wavelengths used in commercial systems are shown in Table 28.6. Pulse energies up to 500 mJ are used with repetition rates up to several hundred hertz.

Pulsed-laser deposition offers several advantages over other PVD methods:

- The interaction of the laser beam and the target produces a plasma consisting of species having high kinetic energy, which enables epitaxial film growth at low substrate temperatures.
- Growth of films having complex stoichiometry can be achieved.
- The irradiation source is outside the deposition chamber allowing flexibility. Multiple chambers can

TABLE 28.6 Excimer Laser Wavelengths

Excimer molecule	Wavelength (nm)
F_2	157
ArF	193
KrCl	222
KrF	248
XeCl	308
XeF	351

use a single laser and the irradiation source can be easily changed.

- Relatively high deposition rates ($>10\text{nm/s}$) can be achieved.
- It is fairly inexpensive.

But it also has several drawbacks:

- It is difficult, at present, to cover large substrates uniformly since the plume peaks in the forward direction.
- The technique is line of sight.
- It is difficult to coat a large number of substrates at once.
- Laser–target interactions can result in the deposition of large (micrometer-sized) particles on the surface of the film. This presents problems if we want to produce multilayer structures.

28.13 ION-BEAM-ASSISTED DEPOSITION

There are two forms of ion-beam-assisted deposition (IBAD). The first is a dual-ion-beam system in which one source is used to sputter a target to provide a source of atoms for deposition (the same process we described in Section 28.10). Simultaneously a second ion beam is aimed at the substrate and bombards the depositing film. In the second configuration, shown in Figure 28.7, an ion source is combined with an evaporation source.

The use of ion bombardment during film growth can modify film properties. For example, IBAD of SiO_2 with 300eV O_2^+ ions during growth can change the refractive index. It is also possible to

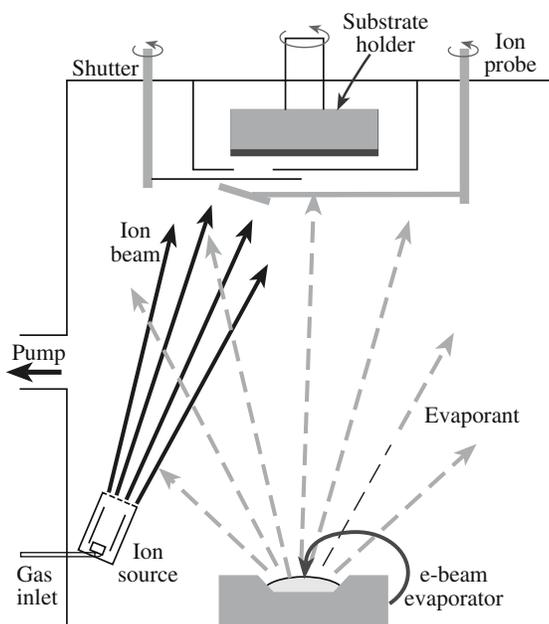


FIGURE 28.7 Ion-beam-assisted deposition system.

- Increase film adhesion
- Modify grain shape
- Induce crystallization

These changes are possible because the incident ion beam may

- Alter surface chemistry
- Create extra nucleation sites
- Increase the surface mobility of the adsorbed atoms
- Raise film temperature leading to higher reaction and diffusion rates

28.14 SUBSTRATES

There are many considerations when choosing a substrate for thin-film growth:

- *Chemical compatibility.* There should be no deleterious reactions between the film and the substrate. For the high temperatures ($\geq 700^\circ\text{C}$) used during the growth of many ceramic thin films this requirement may be quite restrictive.
- *Matched coefficient of thermal expansion (α).* In cases in which the film and substrate are different it will be almost impossible to achieve an exact match in α . A significant difference in α should be avoided because it can cause poor adhesion and cracking of the film. The latter problem is particularly relevant to ceramics, which are often brittle. Brittle materials are particularly weak in tension and therefore it is better if $\alpha_{\text{film}} < \alpha_{\text{substrate}}$; this will put the film in compression.
- *Surface quality.* The surface of the substrate is important because it is here that film nucleation and growth occur. The surface of a single-crystal substrate can contain a variety of defects of different sizes, from emergent dislocations, to surface steps, to scratches due to polishing. The defects are important because they can act as preferential sites for nucleation. Figure 28.8 shows the nucleation of islands of Fe_2O_3 at step edges formed in a Al_2O_3 substrate by high-temperature annealing. This type of orientation mechanism is known as graphoepitaxy, in which the topography of the substrate surface controls the microstructure of the film.
- *Cleanliness.* It is important to ensure that each substrate is cleaned before film deposition. For example, single-crystal MgO substrates are often packaged in mineral oil prior to shipping to avoid the reaction between the MgO and water vapor that results in the formation of $\text{Mg}(\text{OH})_2$. The oil can be removed by soaking in acetone. Many laboratories develop their own in-house cleaning procedures. The main steps involve degreasing in organic solvents, possibly followed by a high-temperature anneal.

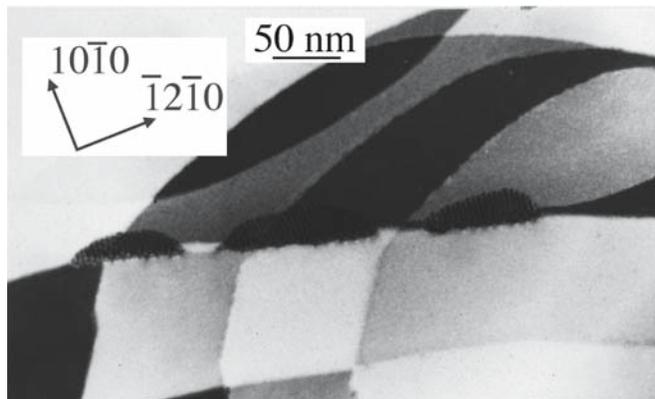


FIGURE 28.8 Growth at surface steps.

- *Substrate homogeneity.* In many single-crystal substrates this is not a problem. But in materials that are heavily twinned, such as LaAlO_3 and LaGaO_3 , twin boundaries that propagate through the substrate can act as nucleation sites. In bicrystal and polycrystal substrates the presence and orientation of the grain boundaries affect film microstructure and properties.

- *Thermal stability.* Phase transformations occurring during heating and cooling can result in the generation of stresses within the film. Perovskite substrates undergo phase transformation.

If we want to form epitaxial films, then we also need to consider the following:

- *Lattice mismatch.* In semiconductor systems lattice mismatches of only a few percent, or less, are desired to reduce the number of dislocations in the film. In ceramic thin films larger mismatches (generally $<15\%$) are tolerated because higher defect densities in the film are acceptable. In some situations a certain number of defects are actually beneficial to film properties (they can provide pinning sites in high-temperature superconductors that can trap magnetic flux lines).
- *Crystal structure.* A close match in the lattice parameters of the film and substrate is one important requirement for epitaxial growth. There must also be a reasonable number of coincident lattice sites on either side of the interface. Frequently, although not always, this means that the film and substrate should have similar crystal structures. The higher the number of coincident sites, the better the chance of good epitaxy.

CHAPTER SUMMARY

Thin films of ceramic materials are important both scientifically and commercially. For example, the operation of semiconductor devices relies on thin dielectric layers. In this chapter we described some of the main techniques used to produce such films. The common feature of all techniques for growing thin films is that we require a vacuum chamber. Deposition may occur at atmospheric pressure (e.g., some versions of CVD), but prior to deposition the chamber was evacuated. The choice of technique is based on several factors, including the type of material being deposited, whether we need an epitaxial layer, and often the cost. The substrate plays an important role in the growth of thin films and thus we need to know the properties of the substrate and how to prepare it. Some of the techniques we described, such as PECVD, are important not only for growing thin films but also for producing nanostructures such as nanowires and nanosprings.

PEOPLE IN HISTORY

Pascal, Blaise (1623–1662) was a French mathematician and philosopher who invented the first digital calculator to help his father, a tax collector. Among his other notable contributions to mathematics and science was laying the foundation for the theory of probability. The SI unit of pressure, the pascal, Pa, is named after him.

Torricelli, Evangelista (1608–1647) was born in Faenza (the home of faience pottery). He invented the barometer and worked in geometry. He died in Florence and the unit of pressure, torr, is named after him.

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EXERCISES

- 28.1 What reactive gases would be suitable for forming the following ceramic thin films by reactive sputtering?: (a) Al₂O₃, (b) TaN, (c) TiC, (d) CdS.
- 28.2 Name two of the ways that you might use to make sputtering targets.
- 28.3 Thin films can grow by three distinct mechanisms. Name the three mechanisms and explain how they differ.
- 28.4 Why is it often desirable to form thin films at the lowest possible substrate temperature?
- 28.5 What advantages are there, if any, of working at high substrate temperature?
- 28.6 What reactant gases might you use for making the following films by CVD?: (a) ZrC, (b) TaN, (c) TiB₂.
- 28.7 Consider the data given below:

Reaction	A	B	C
TiCl ₄ = Ti + 2Cl ₂	180,700	1.8	-34.65
2TiN = 2Ti + N ₂	161,700	—	-45.54
SiCl ₄ = Si + 2Cl ₂	155,600	3.64	-43.90
SiC = Si + C	14,000	1.3	-5.68
C + 2H ₂ = CH ₄	-16,500	12.25	-15.62
$\frac{1}{2}$ H ₂ + $\frac{1}{2}$ Cl ₂ = HCl	-21,770	0.99	-5.22
SiO ₂ = Si + O ₂	215,600	—	-41.50

The values of A, B, and C are given for $\Delta G^0 = A + BT \log T + CT$ (ΔG^0 in cal.). From these data determine whether it would be thermodynamically feasible to form the following ceramic films by CVD at a temperature of 850°C. (a) TiN from the nitridation of TiCl₄, (b) SiC from the reaction between SiCl₄ and methane, and (c) SiO₂ from the oxidation of SiCl₄.

- 28.8 What technique would you use to produce a 100-nm thin film of AlN on silicon? Explain why you chose your technique and its pros and cons.
- 28.9 What technique would you use to produce a 5-nm thin film of BaBiO₃ on MgO? Explain why you chose your technique and its pros and cons.
- 28.10 Which of the techniques described in this chapter is most suitable for producing thin films on large substrates? What is the largest substrate that can be coated?