28

Thin Films and Vapor Deposition

CHAPTER PREVIEW

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 DIFFERENCE BETWEEN THIN FILMS AND THICK FILMS

In the previous chapter 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 $\leq$500 nm in thickness, whereas thick films may be several tens of micrometers in thickness or even thicker depending on 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. PVD techniques rely on excitation of a source (sometimes called the target), which 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 microns per minute (e.g., 2 μm/min), whereas for PVD techniques the growth rate is often orders of magnitude lower (growth rates in the range 0.01–0.03 μm/min are typical). There are other differences that 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 we encounter are listed in Table 28.1. MBE (molecular-beam evaporation) 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, epitaxic, 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.

C.B. Carter and M.G. Norton, *Ceramic Materials: Science and Engineering*,
DOI 10.1007/978-1-4614-3523-5_28,

TABLE 28.1 Some Common Acronyms in Thin-Film Technology

CVD technique	*Chemical vapor deposition*	*PVD technique*	*Physical vapor deposition*
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 now look at each of these characteristics and explain the rationale behind why they are important. The thin film may be crystalline, often epitactic, or sometimes polycrystalline or amorphous. The reason for requiring crystallinity is that for thin films we often make 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 (GBs). In epitactic films, it is often possible to control the types of GB that are produced. Generally, these boundaries are low-angle GBs, 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 $YBa_2Cu_3O_{6+x}$ (YBCO), the value of the superconducting transition temperature depends on the value of x. When x is close to 1.0, the transition temperature is ~90 K. When x is 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 as are 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 others. 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 nonvolatile solid
- 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, particulates form. Under these conditions, the film has a low density and a large number of voids. There are several different geometries for a CVD reactor, and some of them 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).

$$SiCl_4(g) + CH_4(g) \rightarrow SiC\ (s) + 4HCl\ (g) \qquad (28.1)$$

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

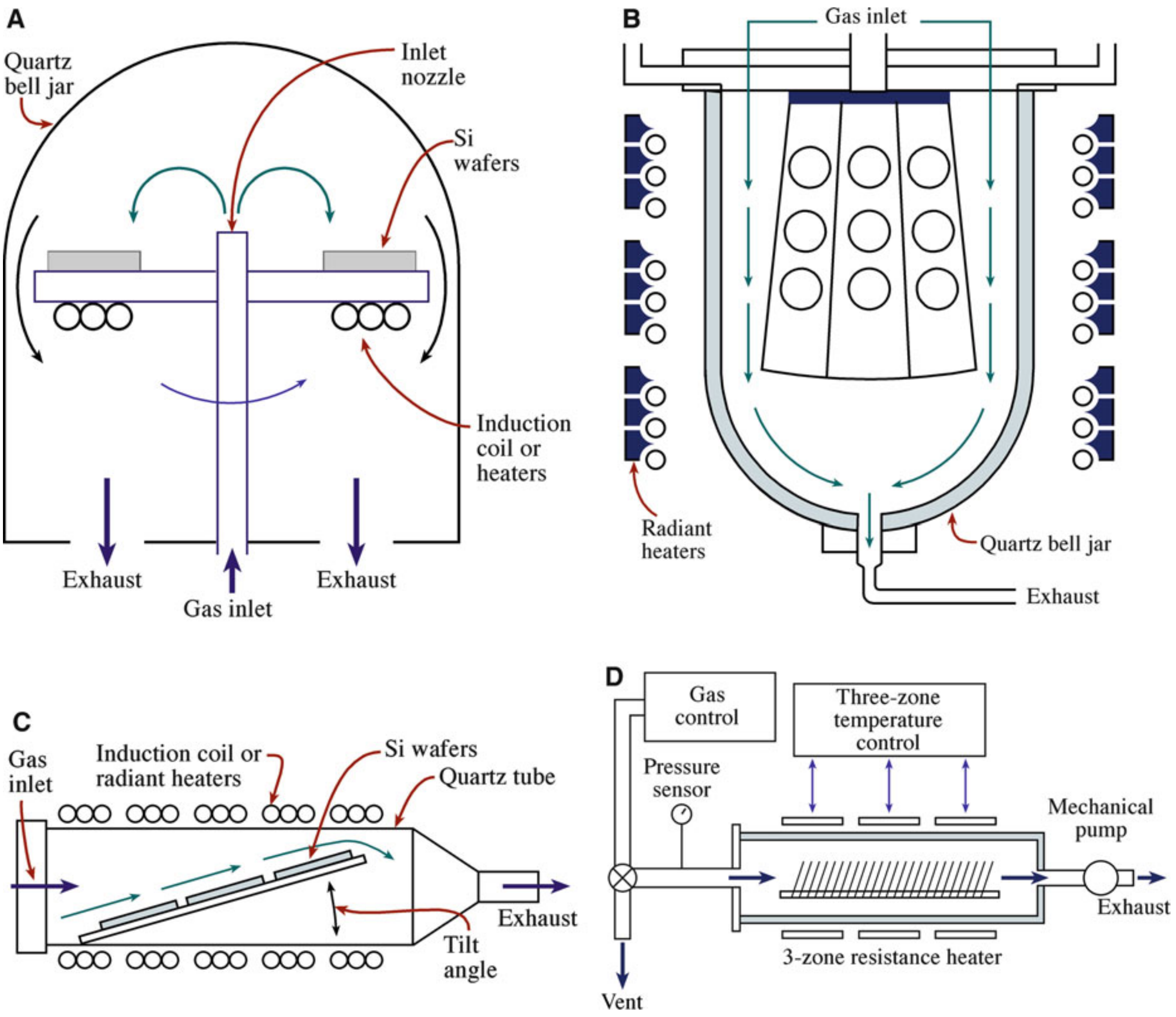

FIGURE 28.1. Examples of chemical vapor deposition (CVD) reactor configurations. (A) pancake, (B) barrel, (C) horizontal, (D) Low-pressure (LP)CVD.

supplied as a high-purity gas directly from a bottle. The reaction between $SiCl_4$ and CH_4 to produce SiC films occurs at 1,400°C. Two aspects of the temperature are important.

- It must be sufficiently high 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.

$TiCl_4\ (g) + CH_4\ (g) \rightarrow TiC\ (s) + 4HCl\ (g)$	(1,000°C)
$BF_3\ (g) + NH_3\ (g) \rightarrow BN\ (s) + 3HF\ (g)$	(1,100°C)
$AlCl_3\ (g) + NH_3\ (g) \rightarrow AlN\ (s) + 3HCl\ (g)$	(1,000°C)

Chemical vapor deposition is one of the most important deposition techniques for forming ceramic films and coatings. We described two examples in Chapter 20, where 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 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!

TABLE 28.2 Examples of Ceramic Films and Coatings Produced by CVD

Film	*Substrate*	*Reactants*	*Deposition temp. (°C)*	*Crystallinity*
Si	Si	Either $SiCl_2H_2$, $SiCl_3H$, or $SiCl_4 + H_2$	1,050–1,200	E
		$SiH_4 + H_2$	600–700	P
Ge	Ge	$GeCl_4$ or $GeH_4 + H_2$	600–900	E
SiC	Si	$SiCl_4$, toluene, H_2	1,100	P
AlN	Sapphire	$AlCl_3$, NH_3, H_2	1,000	E
In_2O_3: Sn	Glass	In-chelate, $(C_4H_9)_2Sn(OOCH_3)_2$, H_2O	500	A
ZnS	GaAs, GaP	Zn, H_2S, H_2	825	E
CdS	GaAs, sapphire	Cd, H_2S, H_2	690	A
Al_2O_3	Si	$Al(CH_3)_3 + O_2$	275–475	A
	Cemented carbide	$AlCl_3$, CO_2, H_2	850–100	A
SiO_2	Si	$SiH_4 + O_2$	450	A
		$SiCl_2H_2 + 2N_2O$	900	
Si_3N_4	SiO_2	$SiCl_2H_2 + NH_3$	~750	A
SiNH	SiO_2	$SiH_4 + NH_3$ (plasma)	300	A
TiO_2	Quartz	$Ti(OC_2H_5)_4 + O_2$	450	A
TiC	Steel	$TiCl_4$, CH_4, H_2	1,000	P
TiN	Steel	$TiCl_4$, N_2, H_2	1,000	P
BN	Steel	BCl_3, NH_3, H_2	1,000	P
TiB_2	Steel	$TiCl_4$, BCl_3, H_2	>800	P

E epitactic, *P* polycrystalline, *A* amorphous

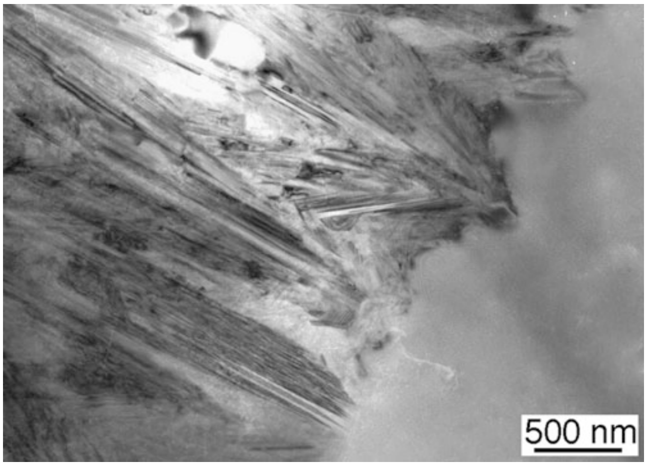

FIGURE 28.2. TEM image showing a polysilicon layer grown on a single-crystal Si rod by CVD.

28.5 THERMODYNAMICS OF CVD

Thermodynamics tells us if a particular chemical reaction is feasible. However, it does not provide any information about the speed of the reaction or film growth rates. Even when a reaction is thermodynamically possible, if it proceeds at very low rates it is not commercially very useful.

We can calculate the standard free energy, ΔG^0, of many reactions using tabulations of thermodynamic data. Consider the reaction between $TiCl_4$ and CH_4.

$$TiCl_4(g) + CH_4(g) \rightarrow TiC\ (s) + 4HCl\ (g) \qquad (28.2)$$

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 1,200 K, we can look up ΔG^0 for the individual reactions below.

$Ti + 2Cl_2 \rightarrow TiCl_4$	$\Delta G_1^0 = -610$ kJ
$C + 2\ H_2 \rightarrow CH_4$	$\Delta G_2^0 = 42$ kJ
$1/2\ H_2 + 1/2\ Cl_2 \rightarrow HCl$	$\Delta G_3^0 = -102$ kJ
$Ti + C \rightarrow TiC$	$\Delta G_4^0 = -171$ kJ

From basic thermodynamics we know:

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

Hence, for the reaction in equation 28.2:

$$\Delta G_r^0 = \left(\Delta G^0{}_4 + \Delta G^0{}_3\right) - \left(\Delta G^0{}_2 + \Delta G^0{}_1\right) \qquad (28.4)$$

The numbers are

$$\begin{aligned} \Delta G_r^0 &= (-171 + 4(-102)) - (42 - 610) \\ &= -11\ \text{kJ} \end{aligned} \qquad (28.5)$$

The negative value of ΔG_r^0 indicates that the reaction proceeds spontaneously at 1,200 K to produce TiC. Consider a similar

ELECTRONIC GRADE SILICON (EGS)

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

calculation at 298 K instead of 1,200 K. The calculated values for ΔG^0 are now:

$Ti + 2Cl_2 \rightarrow TiCl_4$	$\Delta G_1{}^0 = 718$ kJ
$C + 2\,H_2 \rightarrow CH_4$	$\Delta G_2{}^0 = 51$ kJ
$1/2\,H_2 + 1/2\,Cl_2 \rightarrow HCl$	$\Delta G_3{}^0 = 95$ kJ
$Ti + C \rightarrow TiC$	$\Delta G_4{}^0 = 180$ kJ

Therefore, at a temperature of 298 K, the value of $\Delta G_r{}^0$ is +109 kJ. The positive value of $\Delta G_r{}^0$ indicates that the reaction between $TiCl_4$ and CH_4 to form TiC does not proceed spontaneously at room temperature.

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

$$aA(g) + bB(g) = cC(s) + dD(g) \qquad (28.6)$$

The equilibrium constant for this reaction is:

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

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:

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

where (p) is the equilibrium pressure of the reactants and the products. The driving force for growth may be expressed as:

$$\Delta G_r{}^0 = -RT \ln K \qquad (28.9)$$

where R, the gas constant, is 8.314 J K^{-1} 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 is 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 equlibrium constant term is expressed as a logarithm in base 10 (log) rather than as a natural logarithm, ln; then the desired value is $\log K = 0.5$.] When $\ln K$ is very large, the driving force is very large, which tends to produce a polycrystalline film, rather than single crystal epitactic 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.

CVD

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

28.6 CVD 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 out-diffusion during thermal cycling

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

$$SiH_4(g) + O_2(g) \rightarrow SiO_2(s) + 2H_2(g) \qquad (28.10)$$

Above 600°C, water vapor is produced.

$$SiH_4(g) + 2O_2(g) \rightarrow SiO_2(s) + 2H_2O\,(g) \qquad (28.11)$$

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 (B_2H_6) into the gas

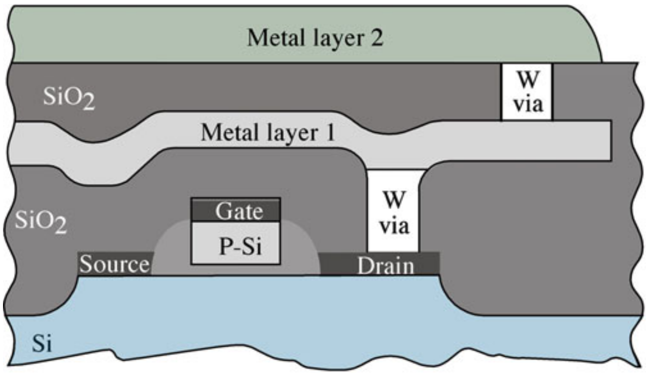

FIGURE 28.3. Cross section of multilayer metallization to a polysilicon gate field effect transistor. The contacts to the source and drain are silicides. Tungsten is used to provide vertical interconnects through vias in the oxide layer.

stream along with SiH_4 and an oxygen source. The chemical reactions for phosphorus-doped oxides are:

$$SiH_4 + O_2 \rightarrow SiO_2 + 2H_2 \qquad (28.12)$$

and

$$4PH_3 + 5O_2 \rightarrow 2P_2O_5 + 6H_2 \qquad (28.13)$$

Phosphorus-doped silica films are used as

- Insulators between metal layers
- Device passivation
- Diffusion sources

One application that we 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 6–8 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.

Si_3N_4, 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 MOS devices to isolate active device regions. The process works as follows: a layer of Si_3N_4 is deposited on the silicon wafer by CVD either by reacting silane and ammonia at temperatures of 700–900°C:

$$3SiH_4 + 4NH_3 \rightarrow Si_3N_4 + 12H_2 \qquad (28.14)$$

or by reacting dichlorosilane and ammonia at 700–800°C.

$$3SiCl_2H_2 + 4NH_3 \rightarrow Si_3N_4 + 6HCl + 6H_2 \qquad (28.15)$$

Like the SiO_2 films described earlier, the Si_3N_4 is amorphous. The exposed regions of the silicon wafer are then oxidized while the areas covered by Si_3N_4 are protected. The oxidizing agent cannot diffuse through the Si_3N_4 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 Si_3N_4 layer is removed.

Si_3N_4 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 CVD

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 0.5–1.0 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 epitactic 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 ($C_2B_{10}H_{12}$).

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 as widely in forming ceramic films. One example of a ceramic film formed by MOCVD is AlN, where the precursors are trimethyl aluminum (TMAl = $Al(CH_3)_3$) and ammonia (NH_3).

$$(CH_3)_3Al\,(g) + NH_3(g) \rightarrow AlN\,(s) + 3CH_4(g) \qquad (28.16)$$

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, Growth Rates

Film	*Temp. (K)*	*Rate (cm/s)*	*Reactants*
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)	1,073–1,273	10^{-5}	C-H_2; C-N_2
CdS	373–573	10^{-6}	Cd-H2S
SiO_2	523	10^{-8}–10^{-6}	$Si(OC_2H_5)_4$; SiH_4-O_2, N_2O
GeO_2	523	10^{-8}–10^{-6}	$Ge(OC_2H_5)_4$; GeH_4-O_2, N_2O
SiO_2/GeO_2	1,273	3×10^{-4}	$SiCl_4$-$GeCl_4$ + O_2
Al_2O_3	523–773	10^{-8}–10^{-7}	$AlCl_3$-O_2
TiO_2	473–673	10^{-8}	$TiCl_4$-O_2
B_2O_3			$B(OC_2H_5)_3$-O_2
Si_3N_4(H)	573–773	10^{-8}–10^{-7}	SiH_4-N_2, NH_3
AlN	1,273	10^{-6}	$SiCl_4$-N_2
GaN	873	10^{-8}–10^{-7}	$GaCl_3$-N_2
TiN	523–1,273	10^{-8}–5×10^{-6}	$TiCl_4$-H_2 + N_2
BN	673–973		B_2H_6-NH_3
SiC	473–773	10^{-8}	SiH_4-C_nH_m
TiC	673–873	5×10^{-8}–10^{-6}	$TiCl_4$-CH_4 + H_2
B_xC	673	10^{-8}–10^{-7}	B_2H_6-CH_4

TABLE 28.4 Hazardous Gases Used in CVD

Gas	*Corrosive*	*Flammable*	*Pyrophoric*	*Toxic*	*Bodily hazard*
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_2H_6)		X	X	X	Respiratory irritation
Dichlorosilane (SiH_2Cl_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				

28.8 CVD SAFETY

Safety issues are particularly important for CVD because 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 closed the plant 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 is 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 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. On the other hand, most compounds dissociate when heated, and therefore the vapor composition is different from that of the source. Consequently, the stoichiometry of the deposited film is also different from that of the source. An example of an oxide that dissociates on heating is ZrO_2.

$$ZrO_2(s) \rightarrow ZrO\ (g)\ + 1/2O_2(g) \qquad (28.17)$$

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; that is, they go from the solid to the vapor without dissociation. For example:

$$AlN\ (s) \rightarrow AlN\ (g) \qquad (28.18)$$

Thus, film stoichiometry would be maintained in the deposit. Several oxides behave in this way (e.g., B_2O_3, GeO, 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 (SEM) and transmission (TEM) electron microscopy 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; it then becomes a neutral atom that returns to the gas to be reionized. A substrate placed facing the cathode is 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 know 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.

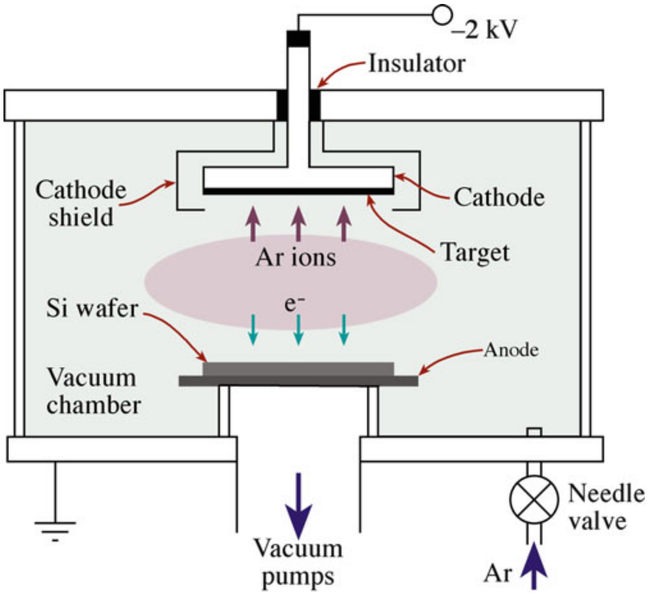

FIGURE 28.4. Sputtering system.

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 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 with energetic species from the plasma.

Ar IN PLASMA FORMATION
Used because of its high mass, which creates a high momentum and more ejected particles from the target.

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

- Reactive sputtering—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 radiofrequency (RF) signal between the electrodes. Typical frequencies are 5–30 MHz.

TABLE 28.5 Ceramic Sputtering Targets

Material	*Applications*
Oxides	
Al_2O_3	Insulation, protective films for mirrors
$BaTiO_3$, $PbTiO_3$	Thin-film capacitors
CeO_2	Antireflection coatings
In_2O_3-SnO_2	Transparent conductors
$LiNbO_3$	Piezoelectric films
SiO_2	Insulation
SiO	Protective films for mirrors, infrared filters
Ta_2O_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, $Gd_3Ga_5O_{12}$)	Magnetic bubble memory devices
YVO_3-Eu_2O_3	Phosphorescent coating on special currency papers
$YBa_2Cu_3O_7$	High-temperature superconductors
Fluorides	
CaF_2, CeF_3, MgF_2, ThF_4, Na_3AlF_6 (cryolite)	Dielectric films for multilayer optical coatings (e.g., antireflection coatings, filters)
Borides	
TiB_2, ZrB_2	Hard, wear-resistant coatings
LaB_6	Thermionic emitters
Carbides	
SiC	High-temperature semiconduction
TiC, TaC, WC	Hard, wear-resistant coatings
Nitrides	
Si_3N_4	Insulation, diffusion barriers
TaN	Thin-film resistors
TiN	Hard coatings
Silicides	
$MoSi_2$, $TaSi_2$, $TiSi_2$, WSi_2	Contacts, diffusion barriers in integrated circuits
Sulfides	
CdS	Photoconductive films
MoS_2, TaS_2	Lubricant films for bearings and moving parts
ZnS	Multilayer optical coatings
Selenides, tellurides	
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, InP) used in the fabrication of LEDs, laser diodes, etc. These inorganic semiconductors are ceramics, so it should not be surprising that the technique can also be used to grow other ceramic thin films (e.g., the high-temperature superconductor $YBa_2Cu_3O_7$). In fact, MBE is ideal for ceramics that have layered structures because it allows precise sequential deposition of single monolayers.

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.

MBE of semiconductors requires the use of an ultra-high vacuum (UHV) chamber (background pressure 10^{-8}–10^{-10} Torr). For oxide ceramics, background pressures of $\leq 10^{-4}$ Torr are more common. The high-vacuum requirement of MBE presents a problem for the growth of many multicomponent oxides (e.g., 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 (e.g., NO_2, atomic O, or O_3) near the surface of the growing film while the background pressure is maintained as low as possible.

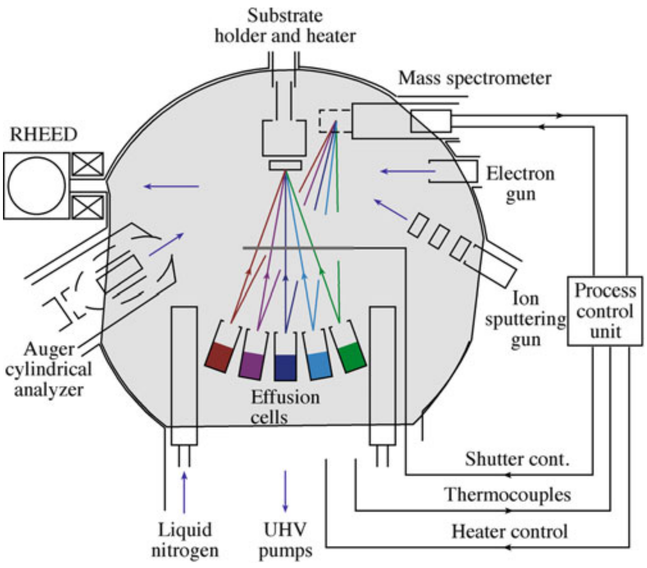

FIGURE 28.5. Molecular beam epitaxy system.

PRESSURE

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 Torr $= 10^5$ Pa).

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

- The equipment is expensive (>$1 million), so the value added must be high.
- Deposition rates are low: ≤ 1 μm/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 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.

PLD GROWTH OF $BaTiO_3$ THIN FILMS CONDITIONS

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

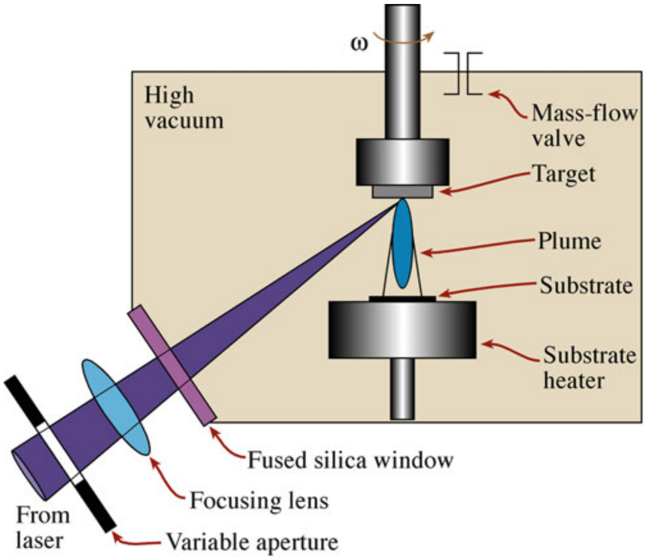

FIGURE 28.6. Pulsed-laser deposition system.

TABLE 28.6 Excimer Laser Wavelengths

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

Excimer lasers operating in the ultraviolet (UV) range are the lasers 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.

PLD 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 epitactic film growth at low substrate temperatures.
- There is growth of films having complex stoichiometry.
- The irradiation source is outside the deposition chamber, allowing flexibility. Multiple chambers can use a single laser, and the irradiation source can be easily changed.
- Relatively high deposition rates (>10 nm/s) can be achieved.
- It is fairly inexpensive.

It also has several drawbacks.

- It is difficult, at present, to cover large substrates uniformly because 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 (micron-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 where 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 300 eV O_2^+ ions during growth can change the refractive index. It is also possible to:

- Increase film adhesion
- Modify grain shape
- Induce crystallization

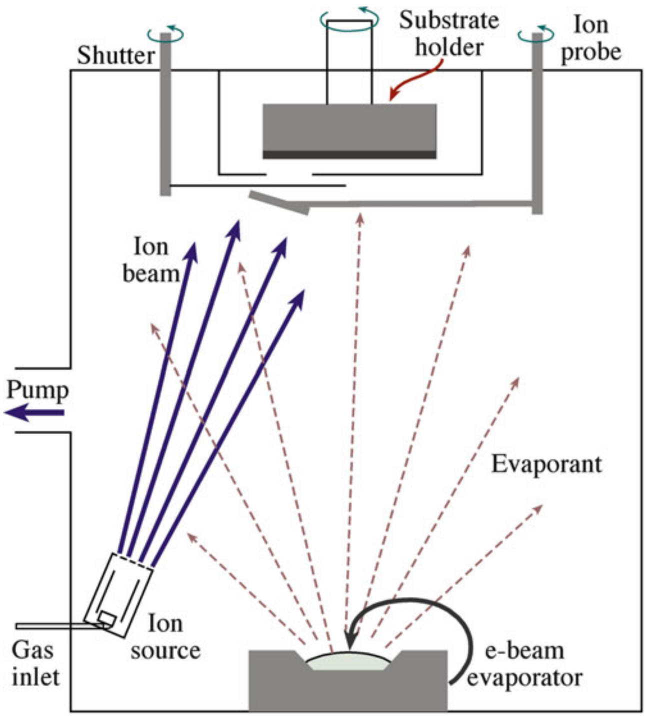

FIGURE 28.7. Ion-beam assisted deposition system.

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 substrate. For the high temperatures ($\geq$700°C) used during the growth of many ceramic thin films, this requirement may be quite restrictive.
- Matched coefficient of thermal expansion (α). In cases where the film and substrate are different, it is 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 $\alpha_{film} < \alpha_{substrate}$, which puts the film in compression.
- Surface quality. The surface of the substrate is important because it is here that film nucleation and growth occurs. 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 an Al_2O_3 substrate by high-temperature annealing. This type of orientation mechanism is known as graphoepitaxy—where the

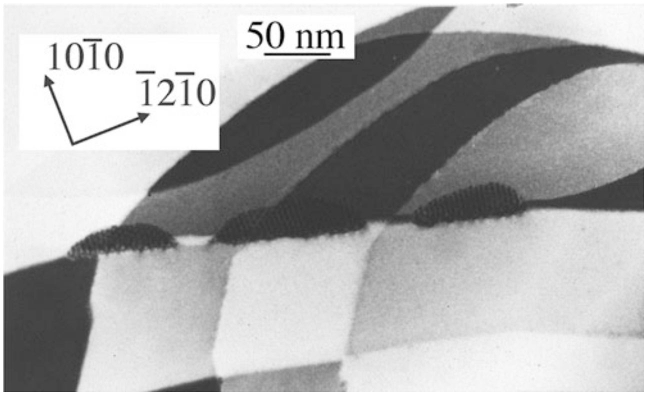

FIGURE 28.8. Growth at surface steps.

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, which results in the formation of $Mg(OH)_2$. 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.
- Substrate homogeneity. In many single-crystal substrates, this is not a problem. In materials that are heavily twinned, however, 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 affects 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 epitactic films, then we also need to consider:

- 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 an important requirement for epitactic 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 is 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 epitactic 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 (e.g., PECVD) are important not only for growing thin films but also in producing nanostructures such as nanowires and nanosprings.

PEOPLE AND 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 most notable contributions to mathematics and science was laying the foundation of 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 faence pottery). He invented the barometer and worked in geometry. He died in Florence. The unit of pressure, torr, is named after him.

EXERCISES

28.1 What reactive gases would be suitable for forming the following ceramic thin films by reactive sputtering?

(a) Al_2O_3; (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? (1) ZrC; (2) TaN; (3) TiB_2.

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
$C + 2\,H_2 = CH_4$	−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 $G^0 = A + BT\log T + CT$ (G^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 $TiCl_4$; (b) SiC from the reaction between $SiCl_4$ and methane; (c) SiO_2 from the oxidation of $SiCl_4$.

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 $BaBiO_3$ 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?

28.11 We suggest that molecular beam epitaxy is often a misnomer. Discuss this viewpoint with examples. (Always reference your sources.)

28.12 If ΔG for the formation of TiC were actually −159 kJ, what would the implications be for the growth of TiC using the method discussed here? Is it particularly important that $TiCl_4$ is used?

28.13 Look up the ΔG values for the reaction in equations 28.10 and 28.11 and explain the reason they are different.

28.14 Using the library or other sources, give examples of oxide deposition, using each of the forms of CVD listed in Section 28.7.

28.15 Sputtering can be used to grow films of yttrium barium copper oxide (YBCO). Discuss the difficulties and how you would overcome them.

28.16 Molecular beam epitaxy can be used to grow oxides. Discuss the state of the art with examples.

28.17 Pulsed laser deposition is our favorite technique for growing oxide films. What is the largest substrate currently being used? What are the thickness limitations? Why do we use different lasers for different materials?

28.18 Ion-beam-assisted deposition has been referred to as (for example) "MBE with a hammer." Discuss this statement.

28.19 Figure 28.1C shows silicon wafers used as a substrate for deposition in a quartz tube. Do we need to control the pO_2 in this situation?

28.20 Figure 28.1C shows a three-zone heater. Give examples of film growth where such a system might be used.

GENERAL REFERENCES

Chrisey DB, Hubler GK (1994) Pulsed laser deposition of thin films. Wiley, New York, A comprehensive survey of PLD and an excellent resource for information about materials grown by this technique

Ohring M (2001) The materials science of thin films, 2nd edn. Academic, Boston, Covers many aspects of thin-film deposition of all types of material. A very useful resource

Pierson HO (1992) Handbook of chemical vapor deposition (CVD): principles, technology, and applications, 2nd edn. Noyes, Park Ridge/New Jersey, Everything you want to know about CVD. Chapter 7 covers CVD of ceramics

Smith DL (1995) Thin-film deposition: principles and practice. McGraw-Hill, New York, A comprehensive handbook on thin-film growth

Thin Solid Films. An international journal devoted to thin films

SPECIFIC REFERENCES

Adams AC (1988) Dielectric and polysilicon film deposition. In: Sze SM (ed) VLSI technology, 2nd edn. McGraw-Hill, New York, Gives an overview of the use of ceramic insulating layers in semiconductor device fabrication

Kubaschewski O, Evans EL, Alcock CB (1967) Metallurgical thermochemistry, 4th edn. Pergamon, Oxford, A good standard thermodynamics text with lots of useful data collected in appendices

Phillips JM (1996) Substrate selection for high-temperature superconducting thin films. J Appl Phys 79:1829