27

Coatings and Thick Films

CHAPTER PREVIEW

The term "thick film" does not just refer to film thickness but rather to layers or a coating made by certain processing techniques. Most of the methods that we describe in this chapter involve suspending ceramic particles either in a solution or in a mixture of organic solvents (known as the *vehicle*). It will be necessary to remove all the volatile material from the coating to produce a dense adherent ceramic layer. Many of the processes described in this chapter are relatively inexpensive (at least compared to those used to produce thin films that we describe in Chapter 28) and simple.

Tape casting is used to produce flat sheets of many different ceramics for applications as substrates, capacitor dielectrics, and fuel cell electrolytes. Some of the techniques described in this chapter, for example, spin coating, are useful only for producing films on flat substrates. However, dip coating and electrophoretic deposition can be used to coat complex shapes. We finish by describing how thick-film circuits are made. In this application the ceramic is used as the substrate onto which the films are deposited and as important ingredients of the pastes that are used to form the circuits. The principle of the technology is not difficult, but controlling the processes may be.

All of these techniques are important in industry and you should know the *language* of thick films, e.g., slurry, slip, and paste.

27.1 DEFINING THICK FILM

A thick film will typically have a thickness in the range 10–25 μm; thin films are usually <500 nm. However, what really distinguishes thick films and thin films, more than just their relative thickness, is the way in which they are produced. Thin films are often deposited using vacuum techniques such as sputtering and molecular beam epitaxy (MBE). We describe these techniques and consider acronyms and hyphens in Chapter 28. Thick films are deposited from a solution or paste, which must be dried and then often sintered to produce the final coating.

There are several advantages of thick-film processing:

- Simple
- Easy to automate
- Rapid
- Inexpensive
- Versatile
- Coating of complex substrates

In addition to describing some of the methods used to apply thick ceramic films to a substrate, we also describe the tape casting process. Films produced by tape casting are not used as coatings but as self-supporting ceramic sheets (down to 25 μm thick) that are widely used in the production of thick-film circuits.

27.2 TAPE CASTING

TAPE CASTING

Band casting and the doctor-blade process are other names.

Tape casting is used to make flat ceramic sheets having a thickness up to about 1 mm. The process was developed during the 1940s for capacitor dielectrics. The production of ceramic capacitors is still one of the most important applications of tape casting.

In tape casting, a slurry (also called a slip) containing a powdered ceramic together with a complex mixture of solvents and binders is spread onto a moving polymer (such as Mylar^{TM}) sheet as shown in Figure 27.1. In the early form of tape casting the slurry was actually spread onto moving plaster-of-Paris plates. The use of a polymer sheet was patented in 1961 and since then the process has

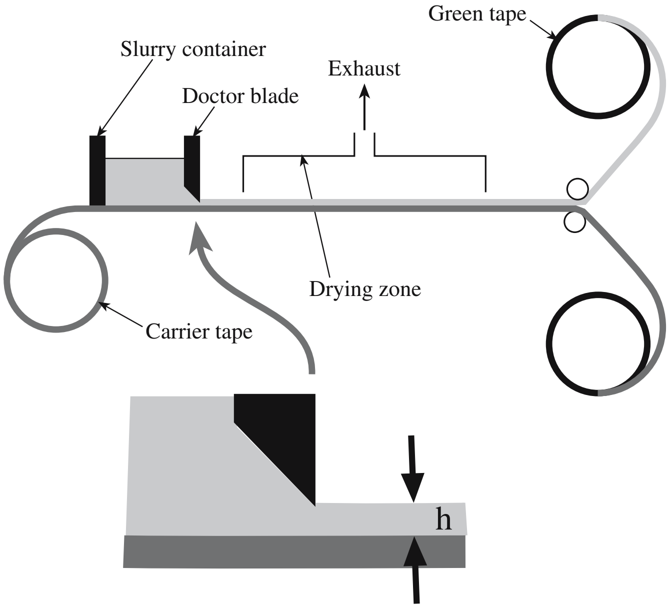

FIGURE 27.1 Schematic diagram of the tape casting process.

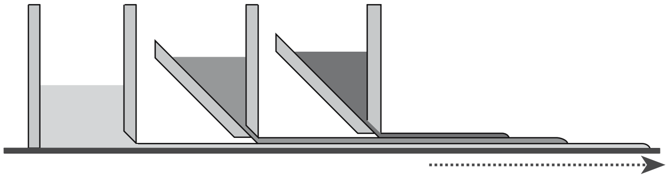

FIGURE 27.2 Illustration of a triple doctor blade for producing multilayer tapes.

not significantly changed. The principle of the process is essentially identical to spreading plaster on a wall, icing on a cake, or painting.

The thickness of the deposited layer is determined by the height of the doctor blade above the polymer sheet. Multilayer films are possible using the approach illustrated in Figure 27.2. The special feature of the doctor blade is that it produces a very uniform thickness. A typical doctor blade assembly is shown in Figure 27.3. The cast tape is dried, peeled from the polymer sheet, and reeled up to wait for further processing. At this stage of the process the tape is flexible because it still contains a high percentage of organics in the form of the polymer binder and is referred to as being "green." This term is used to describe any unfired but shaped ceramic.

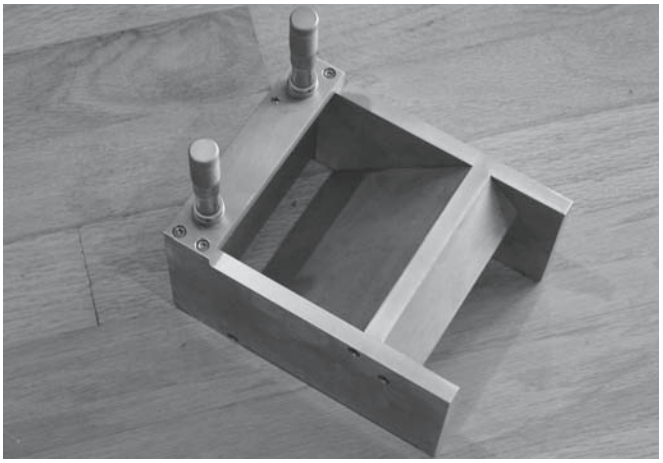

FIGURE 27.3 Typical doctor blade assembly.

The preparation of the slurry is very important. A slurry formulation used in processing alumina sheets for use as substrates for electronic devices is shown in Table 27.1.

- The solvent controls the viscosity of the slurry allowing it to be spread on the polymer sheet.
- The binder holds the ceramic particles together until the tape is sintered and must be removed during the sintering process.
- Plasticizers increase the flexibility of the green tape.
- Dispersants (deflocculants) avoid settling of the powder particles.

Dispersants work by a process known as steric hindrance. The long-chain organic molecules such as those in Menhaden fish oil (a long-chain fatty acid) attach themselves to the ceramic particles with their long molecular tails pointing outward. This orientation prevents the particles from getting too close together and hence reduces the extent of agglomeration or settling. Menhaden fish oil is a natural product and is widely used in the ceramics industry because it is cheap.

TABLE 27.1 Materials for the Preparation of Alumina Slurries for Tape Casting

Milling step	*Material*	*Function*	*wt%*
Stage 1: Mill for 24 hours	Alumina powder	Substrate material	59.6
	Magnesium oxide	Grain growth inhibitor	0.15
	Menhaden fish oil	Dispersant	1.0
	Trichloroethylene	Solvent	23.2
	Ethyl alcohol	Solvent	8.9
Stage 2: Add to above and mill for 24 hours	Poly(vinyl butyral)	Binder	2.4
	Poly(ethylene glycol)	Plasticizer	2.6
	Octyl phthalate	Plasticizer	2.1

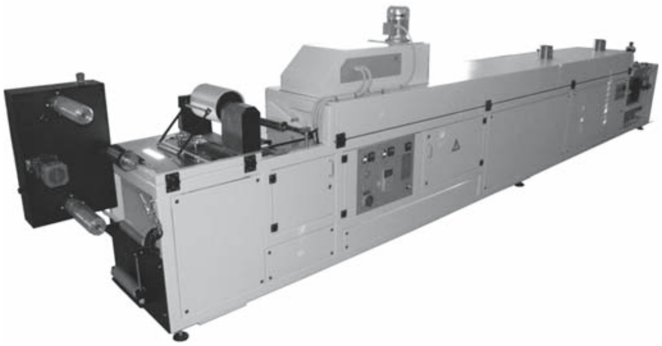

FIGURE 27.4 Example of an industrial tape casting machine.

Extensive shrinkage occurs during drying and firing of the tape because of the large volume fraction of organics in the slurry. For example, when the alumina slurry shown in Table 27.1 is cast to a thickness of 1.50 mm it will dry to produce a 0.75-mm green tape (about a 50% reduction). When sintered, the tape will shrink further to a final thickness of about 0.60 mm.

Figure 27.4 shows a commercial tape-casting machine for the continuous production of ceramic tape. These machines range in size from 2 m to more than 35 m in length and from about 100 mm to more than 1.25 m in width. The size determines the rate at which tapes can be produced. Typical casting speeds are on the order of 0.15 m/min. For quick drying compositions the casting speed can be as high as 2 m/min. In industrial production it is often important to have continuous measurement of the tape thickness. These measurements can be made through a hole in the support plate downstream of the doctor blade. Several different approaches are used commercially: (1) X-ray backscattering from below, (2) X-ray transmission involving instrument heads below and above (a technique commonly used in the aluminum industry to measure the thickness of Al plates), or (3) reflecting visible light at an angle from the top surface of the cast tape. The X-ray transmission method is generally preferred because of its greater accuracy.

Figure 27.5 illustrates the production of an integrated circuit (IC) package that uses tape cast alumina sheets.

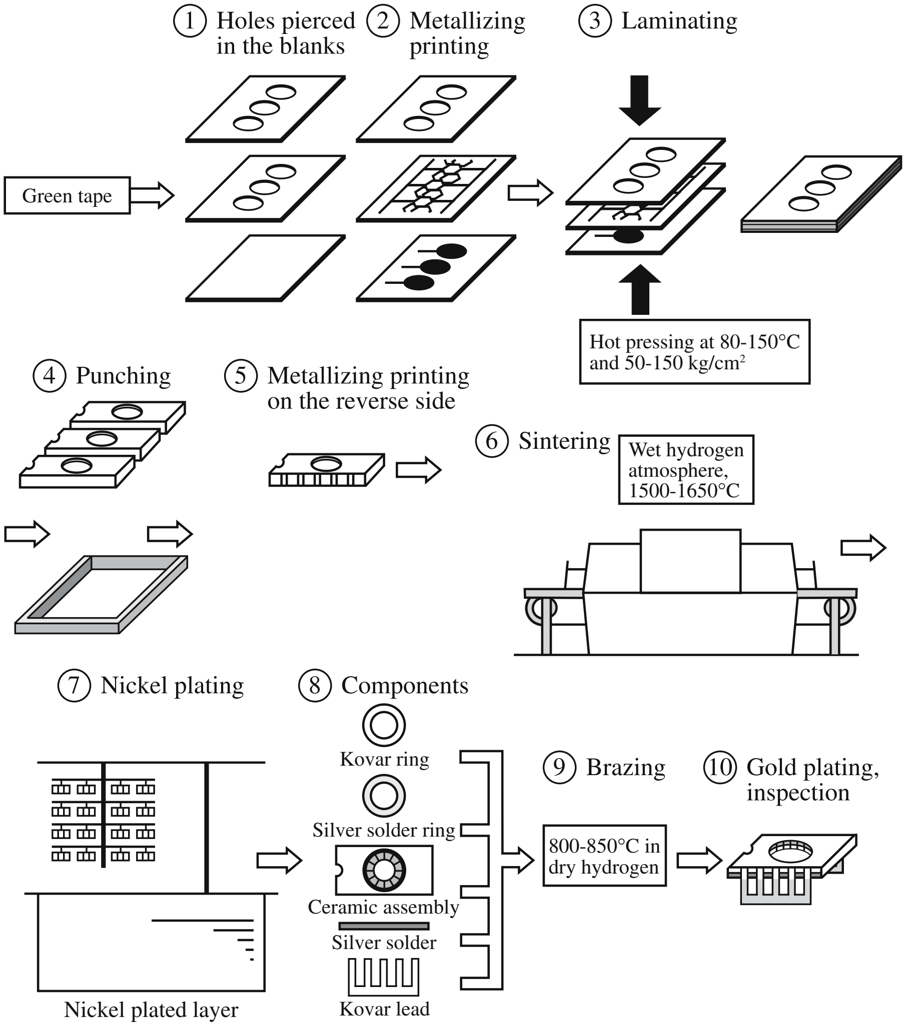

FIGURE 27.5 The steps in the production of an integrated-circuit package.

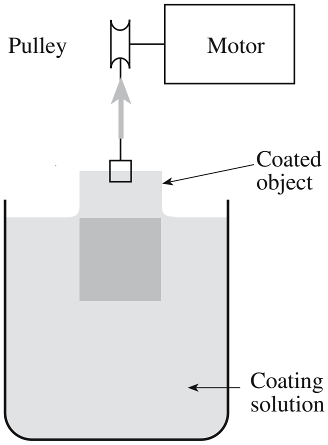

FIGURE 27.6 Schematic of a simple dip coating process.

DIP COATING
The high-tech version of the dipping process used to glaze pottery.

The green tape can easily be punched to produce holes or vias, which are an important part of the processing of IC packages. In addition an ink or paste made of a mixture of metallic powder (tungsten or molybdenum), organic binders, and solvents is screen printed onto the green tape. The tape is then fired in a wet hydrogen atmosphere to produce a strongly adherent metal layer on the sintered alumina. We describe the screen printing process in more detail in Section 27.7.

27.3 DIP COATING

A ceramic film can be formed very easily on a substrate by dip coating as illustrated in Figure 27.6. The starting material usually consists of metal alkoxides, but solutions of metal salts, such as nitrates, may be used instead. The substrate, or object to be coated, is lowered into the solution and withdrawn at rates between 10 and 30 cm/min. It is necessary that the solution wets and spreads over the surface of the substrate and so the contact angle must be low. The final film is obtained after firing the coated object. Dip coating has the following advantages:

- It is simple.
- It is inexpensive.
- Complex shapes can be coated.
- Planar substrates can be coated on both sides at once.

The thickness, *t*, of the liquid film depends on the viscosity, η, of the solution and the speed, *v*, with which the object is withdrawn from the solution and is given by

$$t = 0.944\left(\frac{\eta V}{\gamma_{\mathrm{lv}}}\right)^{1/6}\left(\frac{\eta V}{\rho g}\right)^{1/2} \qquad (27.1)$$

where γ_{lv} is the liquid–vapor interfacial energy, ρ is the density of the solution, and *g* is the acceleration due to gravity. The thickness will, of course, be less in the final fired film due to shrinkage. There are several applications for dip-coated ceramic films as shown in Table 27.2.

27.4 SPIN COATING

Spin coating, like dip coating, starts with a solution that is often a mixture of metal alkoxides. The basic idea is illustrated in Figure 27.7 and there are two variants:

- Static
- Dynamic

In the static spin process, a few volumes of solution is dropped onto the substrate and allowed to spread until it covers most of the surface. Once the liquid has reached a specified diameter the chuck is accelerated to a predetermined speed, on the order of 20,000 rpm.

TABLE 27.2 Applications of Dip Coated Sol-Gel Preparations

Film use	*Composition*	*Conditions*
Mechanical protection	SiO_2	Multistep process; alternating dips and firings at >400°C; increase thickness by 100 nm each cycle
Chemical protection	SiO_2	Great care in drying; minimize cracking and crazing
Transparent electrode	In_2O_3–SnO_2	Single dip process
Antireflecting	Na_2O–B_2O_3–SiO_2	
Specific absorption	TiO_2–SiO_2 Cr_2O_3–SiO_2 Fe_2O_3–SiO_2	
Catalytic		Low temperature gelling below 400°C ensures a porous film that has a high surface area
Photo mode	TiO_2	
Ionic mode	β-Al_2O_3 Ta_2O_5	

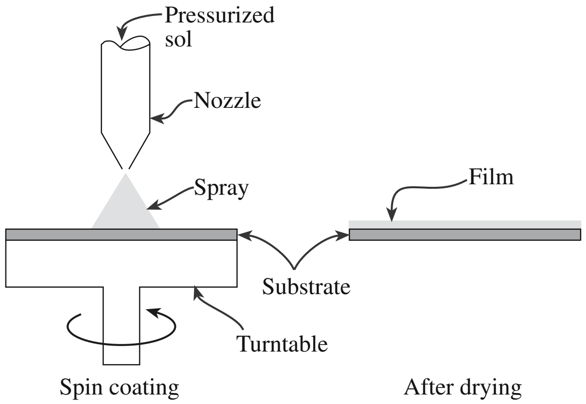

FIGURE 27.7 Schematic of the spin coating process.

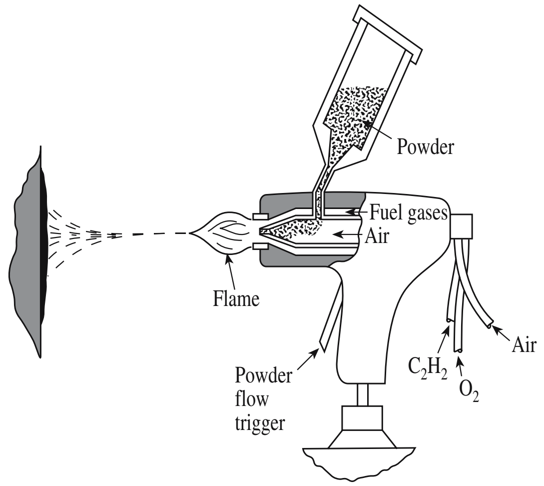

FIGURE 27.8 Thermal spraying with a gas combustion/powder gun.

In the dynamic spin process the solution is dispensed onto the substrate surface, which is spinning at a low speed of about 500 rpm. After the liquid has spread the rotation speed is increased to produce the final film. The dynamic spin process is better for producing uniform coatings on larger diameter substrates.

Spin coating can be used only for single-side coatings and generally is applicable only to fairly simple planar shapes. Also spinning of very large objects is impractical. The thickness of the coating varies inversely with the angular velocity ($\omega^{-2/3}$) of the spin coater and is proportional to the viscosity of the solution ($\eta^{1/3}$). Spin coating is used widely in industry for forming polymer coatings, in particular for the deposition of photoresist layers prior to the patterning of semiconductor devices. Although not widely used for producing ceramic films, spin coating has found some application in forming films of piezoelectric materials for microelectromechanical systems (MEMS).

27.5 SPRAYING

Forming ceramic coatings by spraying is an important industrial process, in particular for applying wear-resistant and thermal-barrier coatings. There are several different types of the spraying process. In thermal spraying, illustrated in Figure 27.8, the powder is melted or softened by passing it through an oxyacetylene flame. A variant of the basic thermal spray process called plasma spraying, which utilizes a plasma heat source, is illustrated in Figure 27.9. The plasma temperature is typically >28,000°C, well

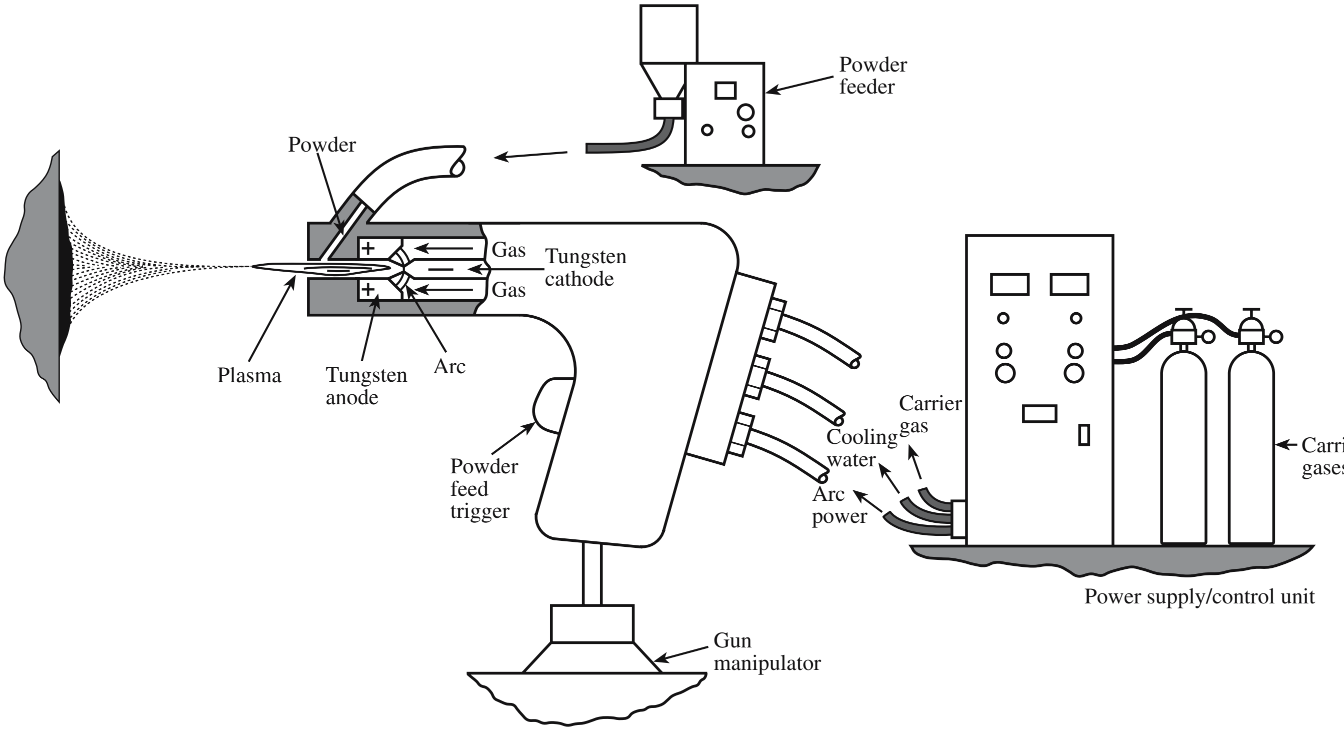

FIGURE 27.9 Thermal spraying using a plasma arc.

SPRAY PAINTING CARS

The paint contains TiO_2 powder.

above that attained in gas combustion processes. The velocity of the plasma/droplet stream that exits the nozzle is usually subsonic, although high-velocity plasma torches with constricted nozzle designs are available. Thermal spray processes are generally suitable for applying any material that melts or becomes plastic in the heating cycle and does not degrade at high temperature.

Plasma spraying is widely used in forming wear-resistant coatings on diesel engine components and for producing thermal barrier coatings on metals for gas turbine engines. The efficiency of gas turbine engines depends on the maximum temperature that can be sustained by the rotor blades during continuous operation. Applying a ceramic coating (called a thermal barrier coating) to the metal can allow the engine temperature to be increased by between 50 and 200°C without the temperature of the metal increasing significantly. There is a corresponding improvement (up to about 12%) in engine efficiency with considerable financial savings. Thermal barrier coatings must have the following properties:

- High coefficient of thermal expansion
- Low thermal conductivity
- Chemically stable in the gas turbine environment
- Thermal shock resistant

EXAMPLE OF ELECTROPHORETIC DEPOSITION

For β-Al_2O_3 coatings the ceramic powder is suspended in an organic liquid mixture composed of nitromethane (CH_3NO_2) and benzoic acid ($C_6H_5CO_2H$). The benzoic acid produces a positive charge on the surface of the β-Al_2O_3 particles by adsorption of protons. The particles can be used to coat a negatively charged electrode.

Yttria-stabilized zirconia (ZrO_2 with between 6 and 8 wt% Y_2O_3) is one of the materials investigated for thermal barrier coatings. Figure 27.10 shows a schematic representation of the cross section of such a coating. An Ni–Cr–Al–Y alloy (called the bond coat in Figure 27.10) provides an adherent interlayer between the metal component and the ceramic coating. Joining metals and ceramics is not a trivial issue and the approach mentioned here is just one of the methods that we mention in this book.

The source material for spraying can be a solution that is forced through a spray gun onto a heated substrate. In this case the spraying is not "thermal" and is more akin to paint spraying. The glass industry uses this approach for depositing conductive layers of SnO_2 on glass.

27.6 ELECTROPHORETIC DEPOSITION

Electrophoresis is the movement of charged particles through a liquid under the influence of an external electric field. Electrophoretic deposition, which is very similar to the electrodeposition process used to form metal coatings, can be used to form a ceramic coating up to 0.6 mm thick on a metallic substrate. The substrate forms one of the electrodes in an electrochemical cell as illustrated in Figure 27.11. The main advantage

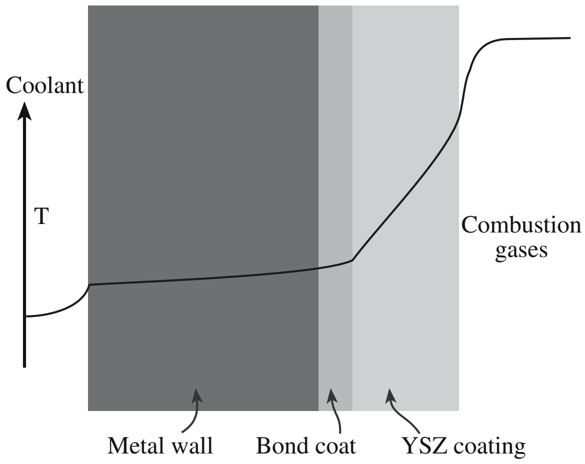

FIGURE 27.10 Schematic representation of a thermal barrier coating. The relative temperatures in the different parts of the coating are indicated.

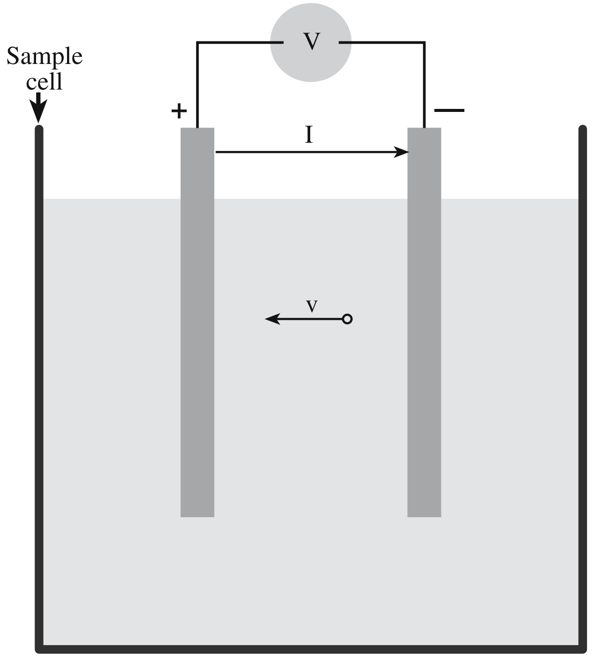

FIGURE 27.11 Schematic diagram of a particle electrophoresis cell.

of electrophoretic deposition is that coatings can be formed on nonplanar objects.

The particles that will form the coating are suspended in a liquid, which produces a surface charge on the particles, for example, by the adsorption of protons. When a particle with charge q is placed in an electric field, E, it experiences a force, F

$$F = qE \tag{27.2}$$

This force accelerates the particle toward the oppositely charged electrode. The particle also experiences a retarding force due to friction as it moves through the fluid. You will recall from Chapter 20 that Stokes' law gives the retarding force due to viscous flow:

$$F = 3\pi\eta dv \tag{27.3}$$

where v is the terminal velocity. We can write this as

$$\nu = \frac{qE}{3\pi\eta d} \tag{27.4}$$

In terms of mobility, μ

$$\mu = \frac{\nu}{E} = \frac{q}{3\pi\eta d} \tag{27.5}$$

From Eq. 27.5 we would expect that particle mobility would be increased for small particles in a solution of a low viscosity. This assumption is not entirely true. For example, the mobility of Li^+ ions in aqueous solution is lower than that of K^+ ions even though $r_{K^+} = 133\,\text{pm}$ compared to $r_{Li^+} = 60\,\text{pm}$. The discrepancy can be accounted for by considering solvation effects. Solvent molecules can cluster around an ion increasing its effective size. Small ions are the source of stronger electric fields than large ions, hence solvation is more extensive in the case of small ions giving them a larger effective size and lower drift velocities. A similar effect can occur for charged ceramic particles moving through a liquid during electrophoretic deposition.

The zeta potential, ζ, which is illustrated in Figure 27.12, is the potential on the surface of the charged particle moving through the liquid.

For a particle in a dilute electrolyte solution ζ is given by

$$\zeta = \frac{q}{2\pi\kappa\varepsilon_0 d} \tag{27.6}$$

where κ is the dielectric constant of the liquid and ε_0 is the permittivity of a vacuum (a universal constant = $8.85 \times 10^{-12}\,\text{F/m}$).

We can now obtain an expression for μ in terms of ζ:

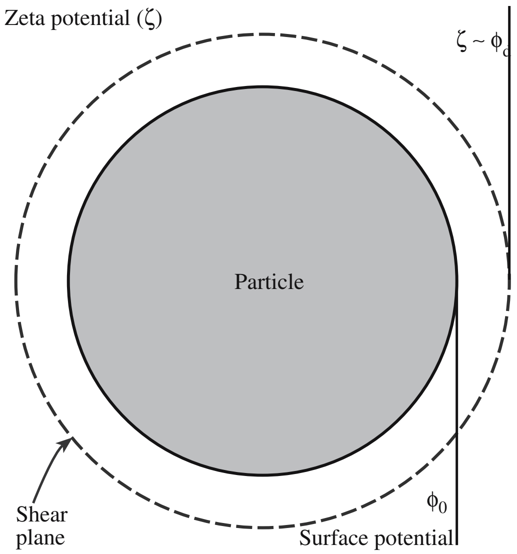

FIGURE 27.12 Illustration of the ζ potential and the effective size of a charged particle.

$$\mu = \frac{2\kappa\varepsilon_0\zeta}{3\eta} \tag{27.7}$$

For concentrated electrolytes we use the Helmholtz–Smuluchowski equation to give us the mobility:

$$\mu = \frac{\kappa\varepsilon_0\zeta}{\eta} \tag{27.8}$$

The important point from both Eqs. 27.7 and 27.8 is that mobility is proportional to κ. For rapid coating we want to use a liquid with a high dielectric constant. The advantage of using aqueous solutions is clear—water has a high dielectric constant. Dielectric constants of some other liquids are given in Table 27.3.

Figure 27.13 shows the electrophoretic mobility of TiO_2 particles in aqueous solutions of potassium nitrate (KNO_3); in this plot, σ_0 is the surface charge density,

TABLE 27.3 Dielectric Constants of Certain Liquids at 25°C and Zero Frequency

Nonpolar molecules		*Polar molecules*	
Methane	1.70 (at 173°C)	Water	78.54 80.37 (20°C)
Carbon tetrachloride	2.274	Ammonia	16.9 22.4 (−33°C)
Cyclohexane	2.105	Hydrogen sulfide	9.26 (−85°C)
Benzene	2.274	Methanol	32.63
		Ethanol	24.30
		Nitrobenzene	34.82

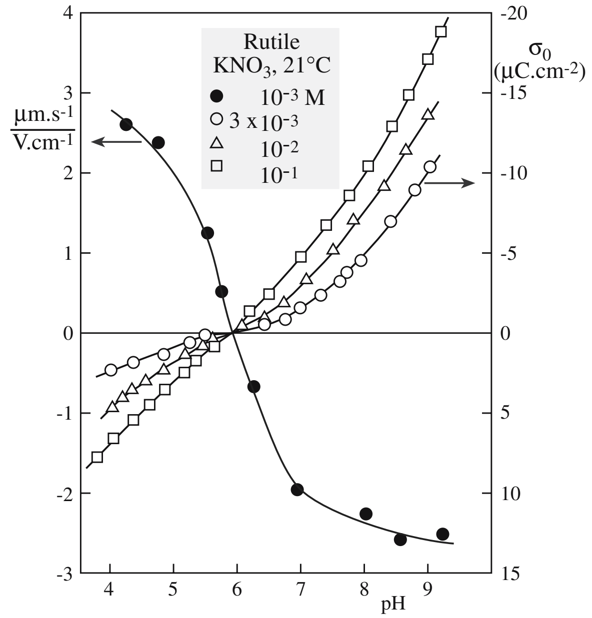

FIGURE 27.13 The surface charge density and electrophoretic mobility as functions of pH for rutile in aqueous solutions of potassium nitrate.

which was measured using the Brunauer, Emmett, and Teller (BET) method. The mobility is a function of the solution pH.

- In acidic solutions the surface of the TiO_2 particles has a positive charge due to cation adsorption.
- In basic solutions the powder particles have a negative charge due to the adsorption of anions.

At a pH of 5.9 the mobility is zero: this point is referred to as the isoelectric point (IEP). At the IEP the ζ potential is zero. Table 27.4 shows IEPs for several different oxides. Acidic oxides such as SiO_2 have low IEPs and basic oxides such as MgO have high IEPs.

TABLE 27.4 Isoelectric Points of Some Oxides

Material	*Nominal composition*	*IEP*
Quartz	SiO_2	2
Soda-lime silica glass	$Na_2O–0.58\ CaO \cdot 3.70\ SiO_2$	2–3
Potassium feldspar	$K_2O \cdot Al_2O_3 \cdot 6SiO_2$	3–5
Zirconia	ZrO_2	4–6
Apatite	$10CaO \cdot 6PO_2 \cdot 2H_2O$	4–6
Tin oxide	SnO_2	4–5
Titania	TiO_2	4–6
Kaolin (edges)	$Al_2O_3 \cdot SiO_2 \cdot 2H_2O$	5–7
Mullite	$3Al_2O_3 \cdot 2SiO_2$	6–8
Chromium oxide	Cr_2O_3	6–7
Hematite	Fe_2O_3	8–9
Zinc oxide	ZnO	9
Alumina (Bayer process)	Al_2O_3	8–9
Calcium carbonate	$CaCO_2$	9–10
Magnesia	MgO	12

27.7 THICK-FILM CIRCUITS

Thick-film circuits are single or multilayer structures produced by depositing a layer, or layers, of a specially formulated paste or ink onto a suitable substrate. Thick-film technology began in the early 1960s when DuPont introduced a thick-film resistor system for application in miniaturized circuits. IBM used thick-film materials in their family of IBM/360 computers. Currently the worldwide market for thick-film circuits and devices is around $14 billion. Most thick-film circuits are still used in electronic applications such as in computers (Figure 27.14).

There are three basic classes of thick-film material (conductors, resistors, and dielectrics) and all have at least one component that is a ceramic. They are supplied in the form of a paste or ink, which contains the following:

- The functional inorganic component or components; this is in the form of a fine powder.
- An organic binder; this is used to provide the green strength.
- A low boiling point organic solvent; this provides the required viscosity to allow the paste to be deposited onto the substrate.

Screen Printing and Processing

Thick-film materials are deposited onto flat substrates by screen printing. The origins of screen printing date back more than 3000 years when the Chinese used "silk screen" printing to deposit multilayered colored patterns onto fabrics. A similar process is still used today to print designs and logos onto T-shirts.

Figure 27.15 shows a schematic diagram of the screen-printing process. The paste is forced through holes in a screen using a rubber squeegee. The viscosity of the ink is determined by the type and amount of organic solvent added to the formulation. Common solvents include pine oil, terpineol, and butyl carbitol acetate. The ideal thick-

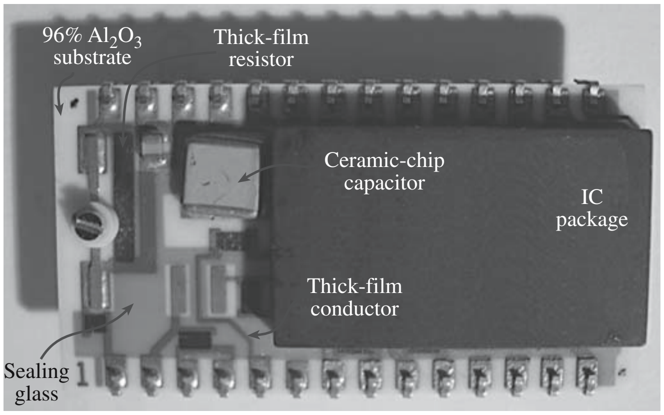

FIGURE 27.14 A typical thick film circuit used in a personal computer showing the different components.

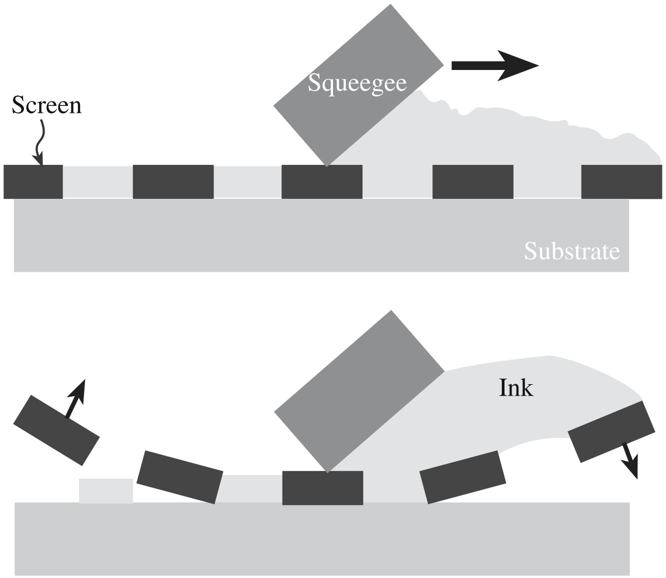

FIGURE 27.15 The screen printing process for depositing thick film circuits. The ink is forced through the screen, which then snaps away leaving a film on the substrate.

film paste should have a low viscosity at a high shear rate produced when the squeegee traverses the screen so that material transfer onto the substrate occurs. The viscosity should remain low for a short time after the squeegee passes and the screen snaps off of the substrate so that the printed film can level to fill in the unevenness from the screen wires. The viscosity should then increase rapidly to a very high value to prevent spreading of the deposited film.

The equipment used to deposit thick-film pastes is similar to that used in printing T-shirts, but for electronic applications much higher precision in the placement of material and thickness control is required. It is possible to produce circuit lines having a width of 5 μm and a thickness of 5 μm. After printing, the substrates (coated with the wet paste) are moved to a drying oven where the low boiling organic solvents are removed. The circuit lines still contain the organic binder, which gives the green strength to the deposited film.

The choice of binder is as important as the choice of solvent. The binder contributes to the overall rheological properties of the paste, but it must be removed completely during firing. Ethyl cellulose is a common binder for air-fired materials. Binders for firing in inert or reducing atmospheres must be chosen carefully to avoid leaving a carbon residue in the fired film; suitable choices include nitrocellulose and copolymers of ethylene and vinyl acetate.

The furnace is a belt furnace with a well defined temperature profile as shown in Figure 27.16. The time at peak temperature is between 6 and 10 minutes during which time the inorganic components sinter together and bond to the substrate.

Substrates for Thick-Film Circuits

Substrates for thick-film circuits generally have to satisfy the following requirements:

- A uniform surface (surface roughness between 20 and 40 μm is typical)
- Minimum distortion or bowing (0.010–0.22 cm/cm)
- The ability to withstand processing temperatures of up to 1000°C
- Tight dimensional tolerances (±0.07–0.10 mm size; ±0.02–0.10 mm thickness)
- Strength
- High thermal conductivity
- High electrical resistivity
- Chemically compatible with paste constituents
- Low dielectric constant
- Inexpensive

Alumina (96% Al_2O_3 with 4% of a glass containing MgO, CaO, and SiO_2) is the most common substrate material because it meets all of the above requirements to an acceptable degree. The substrates themselves are frequently made by tape casting, which we described in Section 27.2.

When a circuit will be used in conditions in which a significant amount of heat will be transferred through the substrate but the thermal conductivity of alumina is not high enough, then alternative materials may be used. For many years the only alternative to Al_2O_3 was beryllia (BeO). The disadvantages of BeO are its cost and high toxicity in both vapor and powder form as encountered in processing. Aluminum nitride (AlN) is another option; it not only has a high thermal conductivity but is closely matched in coefficient of thermal expansion to silicon in the temperature range 25–400°C ($\alpha_{Si} = 4.0$ ppm/°C; $\alpha_{AlN} = 4.3$ ppm/°C). The three substrates are compared in Table 27.5.

Although the properties of AlN make it very well suited for electronic packaging, there have been several problems in commercializing:

- Most commercial AlN substrates have thermal conductivities ~170 $W\,m^{-1}\,K^{-1}$, which is considerably lower than the theoretical thermal conductivity of 320 $W\,m^{-1}\,K^{-1}$.

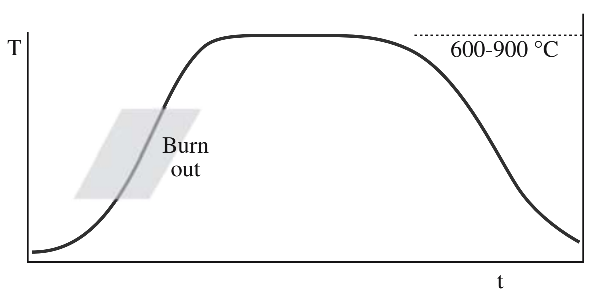

FIGURE 27.16 Typical thick film circuit firing profile.

TABLE 27.5 Properties of Different Substrate Materials (AlN sublimes)

Property	*Units*	*96% Al_2O_3*	*BeO*	*AlN*
Thermal conductivity	$W\,m^{-1}\,K^{-1}$	15–20	230–260	120–210
Coefficient of thermal expansion (RT –400°C)	10^{-6} °C^{-1}	7.2	8.3	4.3
Electrical resistivity	$\Omega \cdot cm$	$>10^{14}$	$>10^{14}$	$>10^{14}$
Dielectric constant (RT at 1 MHz)	Unitless	9.4	6.7	8.6
Dielectric loss (RT at 1 MHz)	Unitless	0.0001	0.0003	0.0002
Dielectric strength	kV/mm	15	10	15
Density	g/cm^3	3.75	2.85	3.3
Melting temperature	°C	2030	2530	2300
Modulus of rupture	MPa	358	280	280–350
Knoop hardness	GPa	19.6	9.8	11.8
Modulus of elasticity	GPa	303	345	331

- AlN powder costs more than four times that of alumina powder.
- The adhesion of pastes designed for alumina is low on AlN unless the surface is preoxidized prior to deposition.

Thick-Film Conductors

The general requirements for thick-film conductors are

- Low electrical resistivity
- Good adhesion to the substrate
- Good line definition

In addition there may be the following considerations:

- Ability to be wire bonded or soldered for external connections
- Resistant to electromigration
- Compatible with other thick film components such as resistors and dielectrics
- Acceptable cost

The functional material in a thick-film conductor is a metal. The important metals and alloys used in thick-film conductors, together with some of their characteristics, are listed in Table 27.6. There are two mechanisms for achieving adhesion of the metal film to the substrate:

- Frit bonding. A small amount (2–10%) of glass powder is added to the paste formulation. During firing the glass softens, wets the substrate, and penetrates into the metal network to develop an interlocking structure. The most common glasses used in frit-bonded conductors are lead borosilicates, e.g., 63 wt% PbO–25 wt% B_2O_3–12 wt% SiO_2.
- Reactive bonding. A small amount (0.1–1%) of CuO or CdO is added to the paste formulation. During firing the oxides react with the alumina substrate to form a copper or cadmium spinel, $CuAl_2O_4$ or $CdAl_2O_4$, respectively.

Frit bonding is the most common method, but there are several advantages to reactive bonding. First, very small amounts of additive are needed, which means that the electrical resistivity of the conductor is kept as low as possible. Second, the surface of the conductor is nearly pure metal, which enhances the attachment of thin Au or Al wires during wire bonding. Some thick-film conductor compositions are termed “mixed bonded” and these contain a glass frit together with a mixture of oxides.

Thick-Film Resistors

The functional phase in thick-film resistors is a mixture of electrically conducting (or semiconducting) ceramic powders such as ruthenium dioxide (RuO_2), bismuth ruthenate ($Bi_2Ru_2O_7$), lead ruthenate ($Pb_2Ru_2O_6$), and Ag–Pd–PdO mixtures for use in air-fired pastes and tantalum nitride (TaN) for nitrogen-fired pastes. The resistance of thick-film resistors is specified in terms of sheet resistance, which has units of ohms/square (Ω/□).

TABLE 27.6 Metals and Alloys Used in Thick Film Conductors

Metal or alloy	*Principal features*
Ag	$ Highest conductivity; Ag ion migrates; tarnishes; seldom in microcircuits; migrates through glass and between conductors
Pd–Ag	$$ Pd inhibits migration but lowers conductivity
Pt–Ag	$$ Smaller quantity of Pt replaces palladium in the binary alloy
Au	$$$$ Highly conductive and chemically inert; reliable bonds to Au wire; high solubility in common solders makes soldering difficult
Pd–Au	$$$$ Compared with Au the solubility in solder is reduced but conductivity is impaired
Pt–Au	$$$$ Reliable solderable alternative to Au; not so conductive
Cu	$ High conductivity; fire in reducing atmospheres to achieve excellent solderability
Ni	$ Can fire in air but not solderable from the furnace

$ lowest cost; $$$$ highest cost.

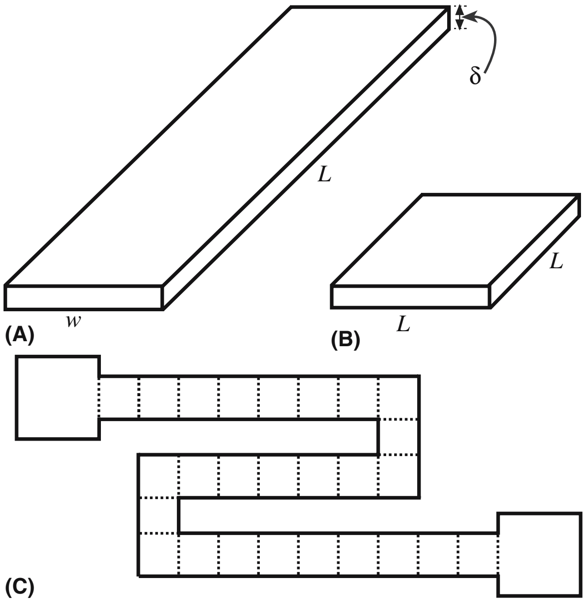

FIGURE 27.17 (a–c) Illustration of sheet resistance.

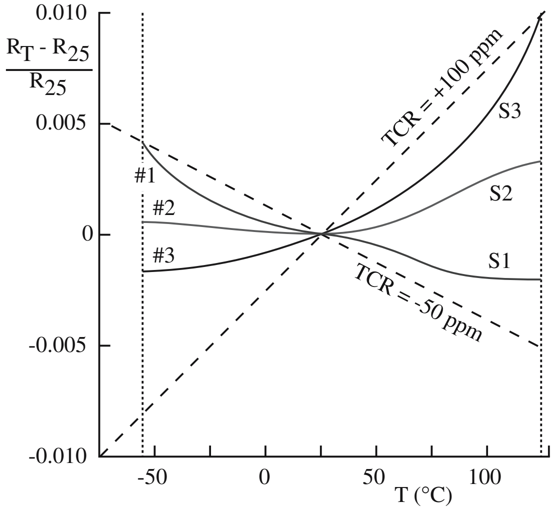

FIGURE 27.18 Typical resistance versus temperature profiles for thick-film resistors.

The concept of sheet resistance is illustrated in Figure 27.17a, which shows a sheet resistor of length l, width w, and thickness d, having a resistance, R given by

$$R = \frac{\rho l}{dw} \tag{27.9}$$

where ρ is the resistivity. If the resistor is square in shape, as in Figure 27.17b, then $l = w$ and Eq. 27.9 becomes

$$R = \frac{\rho}{d} \tag{27.10}$$

For a given material and thickness, all square sheets have the same resistance independent of the size of the square. The resistance of such squares is known as the sheet resistance. Figure 27.17c shows a complex thick-film resistor configuration, but the resistance can easily be determined by dividing it into squares, counting the number of squares per strip, and multiplying by the sheet resistance.

SHEET RESISTANCE

It depends only on the thickness of the resistor and its resistivity.

Thick-film resistors are available with sheet resistance values in the range from 0.1 to 10 M Ω/□. By blending different quantities of conductive material and an electrically insulating glass the resistivity is controlled. For a high sheet resistance formulation the ratio of conductor to glass would be about 70/30.

An important parameter for thick-film resistors is their temperature coefficient of resistivity (TCR), which is a measure of how much the resistance changes with temperature. It is defined as the slope of the change in resistance ($\Delta R/R$) versus temperature as illustrated in Figure 27.18. The TCR limits specified for a particular formulation are the slopes of the two lines passing through the reference points on the curve that bound the resistance deviation. Typically the reference temperature is 25°C and the temperature range is −55°C to +125°C. TCR values for thick-film resistors are typically less than ±100 ppm/°C.

Resistor patterns are designed so that the average value of the fired resistor is lower than the required value. The final resistor is then trimmed using a laser, or an abrasive jet, to remove material and increase the resistance to within ±1% of the desired value.

Thick-Film Dielectrics

Dielectrics are used in several difficult applications in thick-film circuits:

- To isolate circuit lines in multilayer structures
- As a dielectric layer in thick-film capacitors
- To encapsulate circuit components

For multilayer applications the functional material is commonly a glass or a glass-ceramic. It must have a low dielectric constant and be thermal expansion matched to the substrate to prevent stresses that can cause the substrate to bow. The film must also be stable as it may be subjected to many firing cycles in the fabrication of a multilayer structure.

For thick-film capacitor applications the dielectric composition will contain a material with a high dielectric constant such as barium titanate. Encapsulants are used to protect resistors from harmful environmental conditions such as high humidity and reactive organic solvents, and to protect silver-containing conductors from silver migration. The glass is chosen so that it can be fired at low temperatures to avoid significant refiring of the thick-film resistors (which would change their resistance values). Typical firing temperatures for encapsulant glasses are ~500°C. Most glass formulations used in the thick-film industry are proprietary. But to achieve low softening temperatures the glass used for encapsulation will probably contain a significant amount of either PbO or B_2O_3.

CHAPTER SUMMARY

The term thick-film refers to layers and coatings made by certain types of processing techniques. Such films are usually not prepared using vacuum conditions. In this chapter we described most of the techniques that are used to produce thick ceramic films. Some of these processes are extremely simple and inexpensive such as dip coating, which can be accomplished, at a minimum, with simply a beaker and a pair of tweezers. However, processes such as thermal spraying require specialized equipment.

In this chapter we described tape casting. This process is used to make flat sheets. Although this is a means of shaping and could have been described in the "shaping" chapter we described it here because it shares a common feature with the other thick film coating methods: it uses a slurry. It also is the process most often used to make ceramic substrates for thick-film circuits. Ceramics are a major component of thick-film circuits. Even in thick-film conductors, ceramics are important in ensuring adhesion between the metal layer and the substrate (which is invariably also a ceramic).

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EXERCISES

27.1 The slurry formulation for tape casting barium titanate sheets consists of the following ingredients: barium titanate powder, phosphate ester, methyl ethyl ketone, ethanol, acrylic resin, benzyl butyl phthalate, and poly(ethylene glycol). (a) Explain the function that each of the ingredients has in the formulation. (b) What would be the usual amounts (in wt%) of each of the ingredients in a typical tape cast formulation?

27.2 Explain why shrinkage of a cast tape occurs during drying and firing. Which of the ingredients in the above formulation would you expect to be lost at each stage of the process? Justify your answer.

27.3 Of the methods described in this chapter which one would you choose to produce a uniform 10 μm coating of $BaTiO_3$ on a 5-cm-diameter silicon wafer? Justify your choice.

27.4 Of the methods described in this chapter which one would you choose to produce a uniform 100 μm coating of Al_2O_3 on a 5-mm-diameter steel rod? Justify your choice.

27.5 Would thermal spraying be a suitable technique for forming thick films of aluminum nitride (AlN)? Explain the reasoning for your answer.

27.6 Alumina substrates for electronic packaging usually contain 96% Al_2O_3 and the remaining 4% is a mixture of $CaO–MgO–SiO_2$. Why do you think these constituents are added to the alumina and what effect, if any, do you think they will have on the properties of a 96% alumina substrate compared to a 99.5% alumina substrate?

27.7 In glass formulations used in thick-film inks alkali metal constituents are avoided. Why?

27.8 Who are the major vendors for thick-film materials?

27.9 Rank the thick-film conductors in Table 27.6 in terms of electrical conductivity starting with the most conductive. Is the trend consistent with their cost?

27.10 Figure 27.14 shows a thick-film circuit. (a) What is the role of the sealing glass? (b) Why is it green? (c) What properties are important for the sealing glass?