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Ceramic Thin Films: Fabrication and Applications

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Ceramics are a distinct class of materials whose properties range from extreme hardness to unique electrical behavior. New methods of creating thin films of complex oxides and electronic ceramics allow the integration of these properties with semiconductor technology and raise the possibility of a new range of electronic devices.

POLYCRYSTALLINE CERAMICS HAVE BEEN WIDELY RECOGnized as important materials for both structural and electrical applications. Structural ceramics based on oxides, nitrides, and carbides are finding increasing use as mechanical components in engines and other machinery (*1*). Electrical ceramics range from passive oxides such as alumina (Al_2O_3) and silica (SiO_2) which are used as substrates and insulators in electronic circuits (*2*), to "active" oxygen-ion conducting zirconia (ZrO_2) which forms the basis for high-temperature oxygen sensors in automobile engines (*3*). More complex perovskite compounds such as barium titanate ($BaTiO_3$) and lead zirconate titanate are used in capacitors, electrically driven mechanical resonators, or electrically controlled optical switches (*4*). Such devices are widely employed as ultrasonic transducers and pressure sensors in medicine and engineering. The most recent development in electronic ceramics has been that of high critical temperature ceramic superconductors such as $YBa_2Cu_3O_{7-\delta}$ (*5*).

Ceramic coatings of alumina, silica, and titanium nitride prepared by the plasma spraying of powders onto a surface through a high-temperature gas plasma have long been recognized as an important method of resisting corrosion and minimizing wear (*6*). In recent years, other methods have been developed for the fabrication of thin films of more complex oxide ceramics. This article explores the major techniques used for this purpose and examines the opportunities that result for novel electronic devices and sensors.

The challenges encountered in fabricating thin ceramic films arise from the complexity of the materials in both composition and structure. For example, ferroelectric or piezoelectric properties arise in crystals when an internal electric polarization exists that can be modified by the application of mechanical or electrical stress (*7*). A mechanical stress then induces an electrical potential difference between electrodes or an electrical field causes a mechanical distortion of the crystal. The quartz phonograph pickup is the most commonly recognized application of this phenomenon. The effect arises in materials that have an asymmetric crystalline structure such that the center of electrical charge within the unit cell does not coincide with the center of mass. Examples of such materials are zinc oxide (ZnO), barium titanate, or lead zirconate titanate ($PbZrO_3$:$PbTiO_3$ often known as PZT). For the effects to be large the composition and the crystallographic structure of the crystal must be precisely defined. However, it is difficult to grow single crystals of these materials and they are often used as randomly oriented polycrystalline ceramics. In this case a net dipole orientation is induced by external "poling" with a high electrical field analogous to magnetizing a permanent magnet. Growth of a material as a thin film cannot only be used to fabricate complex ceramics on a scale compatible with semiconductor microcircuits, but can also provide a unique opportunity to create an internal crystallographic texture or epitaxial morphology (*8*). Figure 1 shows a film of zinc oxide that has been grown with the *c*-axis of the crystal structure tilted at a specific angle to a substrate (*9*). This allows specific combinations of longitudinal and shear acoustic waves to be generated for particular applications of an ultrasonic transducer (*10*).

A second form of crystalline complexity arises in the polycrystalline high critical temperature ceramic superconductors represented by $YBa_2Cu_3O_{7-\delta}$. The major factor that currently limits the use of these ceramic materials as practical superconductors is the current carrying capacity which is expressed as the critical current density J_c (amperes per square centimeter). This is primarily determined by the grain boundaries between the crystallites and secondarily by their alignment (*11*). The highest value of critical current in a ceramic superconductor has been reported in a thin film sample where the deposition process has been used to minimize grain boundaries and to produce a high degree of texture (*12*).

Integration of thin films of electronic ceramics with semiconductor technology has a number of interesting features. First, it broadens the range of sensing and signal processing elements available to the semiconductor designer, partly by enabling the amplifiers and conventional electronics required by the sensor to be

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integrated onto the same silicon chip (*13*). Second, new devices are possible. There is currently much interest in the development of a nonvolatile semiconductor memory element made with ferroelectric films (*14*). Low-density memories (256 and 1024 bits of stored information) have been fabricated that use the polarization field of PZT to retain the logic state of an associated memory device when the external power is removed (*15*). Such solid-state ferroelectric memories would have widespread application as nonvolatile radiation-hard memory elements in telephone, industrial, and military equipment (*16*).

The challenge is therefore to create thin films of complex oxide materials having a precise composition with a known crystallographic structure. The films need to be prepared on a range of metallizations and possibly oriented with respect to commonly used semiconductor substrates. The functional properties of the bulk ceramic need to be reproduced in the thin film.

Methods of Film Fabrication

Thin film technologies for the fabrication of complex electronic oxides fall into two broad areas (*17, 18*): (i) physical techniques, which include thermal and electron beam evaporation; dc, radio frequency, and ion beam sputtering; and laser ablation; and (ii) chemical techniques, which include spray pyrolysis, chemical vapor deposition, and sol-gel processes.

In each case, the objective is to provide an appropriate flux of atoms onto a substrate such that the required compound grows controllably on the surface. The source may be a bulk material of composition similar to that desired in the film, or solutions or vapor streams containing the required atoms with the reaction forming the compound occurring at the substrate itself.

Physical methods. In thermal evaporation, the source material is heated to above its vaporization point in a vacuum either by resistive heating or by the impact of an electron beam. This is a well-established industrial process for metals (Cu or Al), simple oxides such as silica (SiO_2), silicon monoxide (SiO), or yttrium oxide (Y_2O_3), and for simple compounds such as zinc sulfide (*17*). Figure 2 shows a schematic of a multilayer electroluminescent display device prepared primarily by sequential electron beam deposition through appropriate masks (*19*).

Radio frequency and dc sputtering. Sputtering describes the physical transfer of atoms from a target to a substrate as a result of momentum transfer. Normally this occurs due to the bombardment of the target by high-energy ions. Some of the processes involved are illustrated in Fig. 3. The ions are created in a dc or radio-frequency gas plasma excited in the space between the target and the substrate, or can be directly energized in a separate ion source. Radio-frequency (rf) excitation is used for insulating targets in order that electrons and positive ions impact on the target surface on alternate half cycles of the power cycle. This nullifies the surface charge that otherwise builds up on the target as deposition proceeds. In the last 10 years effective methods to increase deposition rates and to control deleterious effects arising from electron bombardment of the substrate have been devised using static magnetic fields. The technology of magnetron sputtering is now well established (*20*), and the deposition rates for metals such as copper can be as high as 2 μm/min. Large-scale magnetron systems are used for metallizing automotive components and window glass as well as being a vital technology in semiconductor processing.

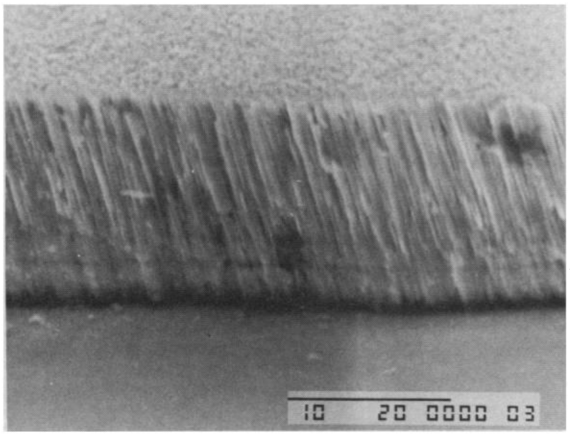

Fig. 1. Zinc oxide films with *c*-axis growth tilted with respect to the silicon substrate (*9*). The figure shows the crystal morphology at an edge which crosses the center of the picture.

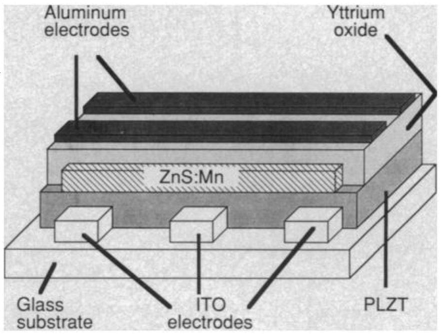

Fig. 2. The structure of a thin film electroluminescent display device where the layers are created by electron beam deposition of the various compounds through different masks. In this case, the lanthum-doped PZT layer (PLZT) was created by a sol-gel process.

In conventional oxide film fabrication, oxide targets are rf-sputtered directly with controlled mixtures of argon and oxygen (*21*). However, the reactive sputtering of multicomponent metal targets in a high partial pressure of oxygen has been successful as a method for the fabrication of complex oxide films (*22*). This process is accomplished in several stages and in a sense can be described as "chemistry within a plasma." The probability of sputtering of a given atomic species is described by the sputtering yield $S(E)$ (*23*)

$$S(E) = \alpha^*[m_t m_g E]/[(m_t + m_g)B(E)] \qquad (1)$$

where m_t and m_g are the masses of the target atoms and the incident ions, respectively, E is the energy of the incident ion, and $B(E)$ is the binding energy of atoms within the target. The parameter α^* varies with the ratio of the two masses. The binding energy $B(E)$ of oxides is large compared to that of metals and the mass of oxygen is less than the mass of argon so that the sputtering rates for oxides in oxygen are orders of magnitude less (0.02 μm/min) than those for metals in argon. However, despite this, the reactive sputtering of metals often affords greater reproducibility in the final oxide film since a reproducible target surface can be maintained for a metal, or at least the surface becomes coated with a uniform oxide. Complex oxides such as ferroelectric PZT can also be reactively sputtered from a three-component metal (Pb, Ti, Zr) target. A target used for this purpose is shown in Fig. 4 (*24*). In order to achieve the correct film composition, the area of each metal within the target is weighted by the calculated sputtering yield. Conditions at the target define the rate at which atoms are contributed to the plasma, but growth of the film on the substrate depends on the diffusion and mixing of the ejected species within the target-substrate region, and on the mechanisms of nucleation and growth on the substrate itself. The latter depends partly on the crystallographic nature of the substrate, and partly on the thermodynamic parameters of the deposit. For example, in the case of lead titanate ($PbTiO_3$), single crystal substrates such as magnesium oxide (MgO) or epitaxially grown magnesium aluminate ($MgAl_2O_4$) have a lattice spacing

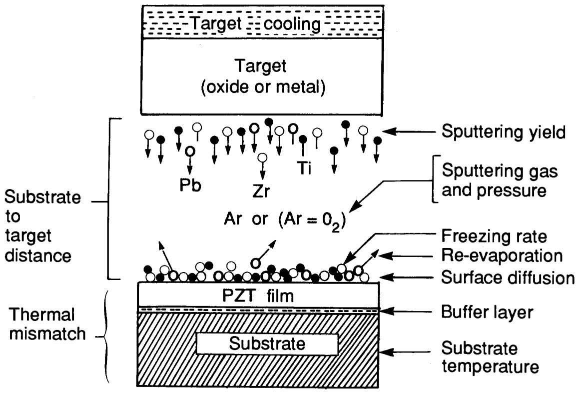

Fig. 3. Processes that occur during reactive sputter deposition of a complex multicomponent oxide. The growth of the film is affected by events within the plasma and on the substrate surface.

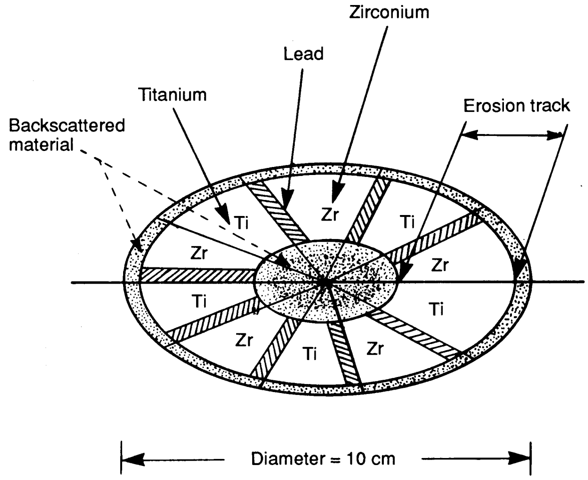

Fig. 4. A multicomponent metal target containing pie-shaped sections of lead, zirconium, and titanium used for the reactive sputtering of $PbZrO_3$: $PbTiO_3$ (*22*). [Copyright 1988, reprinted with permission of the Institute of Electrical and Electronic Engineers]

which corresponds to a specific lattice spacing in the crystal structure of lead titanate. The fact that atoms in the layer "fit" to certain crystallographic orientations on the substrate can induce oriented or epitaxial growth in the film. Extensive studies of such phenomena have been made by Japanese workers (*25*) and the modeling of crystal growth processes in the film is an important and developing field. For most oxide films, the deposition is made at a substrate temperature of the order of 200° to 400°C which is sufficient to introduce incipient crystallization, but this is followed by an anneal in oxygen at 400° to 600°C. The advantage of this procedure is that the lower substrate temperature minimizes re-evaporation of materials having low sticking coefficients during the deposition, and as long as all elements are present in stoichiometric or excess quantities (*26*), post-deposition annealing serves both to bring the composition to equilibrium through the volatilization of excess components such as lead, and to develop a stoichiometric concentration of oxygen. Such oxygen annealing is vital in the case of high-temperature superconductors (*27*).

Sputtering is, in principle, an improvement over evaporation in that all elements of the compound sputter in some equilibrium fashion from the target surface as the target face erodes. However, particularly in oxide targets, as the oxygen stoichiometry of the target varies, or other physical changes occur, the average or local binding energy $B(E)$ can change significantly and modify the film composition.

Laser ablation. High-power lasers can be used to evaporate ceramics at ambient pressures, or in controlled partial pressures of oxygen (*28*). A laser beam focused on the surface of a target evaporates material onto a neighboring substrate. The incident energy is localized within an optical absorption length and there is a high probability that all species within a small volume are vaporized simultaneously. Substrate effects are likely to be similar to sputtering, but the target composition can be reproduced more closely. This technique has been extremely effective for high transition temperature (T_c) superconductors (*29*).

The advantage of vacuum techniques are that they are compatible with much semiconductor integrated circuit processing. If in situ crystallization can be induced the properties of the oxide films are unparalleled, although sputtering yields for many oxides seem to set a natural limit on deposition rates of the order of 1 μm/hour. A significant disadvantage is that at physically realistic substrate temperatures, controlled either by the achievable substrate temperature or by the volatilization of film components after condensation, films deposit with an amorphous crystallographic structure and secondary crystallization has to be induced by a high-temperature post-deposition anneal. This is slow, intrinsically unsatisfying, and introduces other processing problems. Other problems are that vacuum equipment is capital intensive and is generally only capable of uniform deposition primarily along the line of sight from the target. In recent years, chemical methods have been examined to alleviate some of these difficulties.

Chemical methods: Spray pyrolysis. The simplest form of chemical deposition is that of spray pyrolysis, in which chemical vapor streams are reacted at a heated substrate. A common example is that of transparent stannic oxide conducting coatings prepared on glass. $SnCl_4$ vapor is reacted with steam at the surface of a glass plate held at 600°C to form SnO_2 with the release of HCl. For more complex compounds, the nonequilibrium nature of this type of reaction and the difficulties of controlling it make the process useful only in a limited number of cases although the pyrolysis of organometallic compounds can extend the technique (*30*).

Chemical vapor deposition. In principle, chemical vapor deposition (CVD) has a very strong potential for the fabrication of all types of oxide and nitride films. For PZT, volatile reactants such as metal-organic lead compounds, titanium tetrachloride, or zirconyl chloride are transported through a reaction chamber by a carrier gas such that the desired material grows in an equilibrium manner on a heated substrate (*31*). For this and other compounds, the process can be enhanced by a gas plasma excited in the vicinity of the substrate [plasma enhanced–CVD (PECVD)] (*18*). The epitaxial growth of semiconductors such as gallium arsenide (GaAs) by this process is now a well-established industrial process, and significant progress has been achieved with materials such as zirconia and aluminum nitride. For example, textured films of AlN of thickness >300 μm have been grown at temperatures <800°C at deposition rates of several micrometers per minute (*32*). Variations can be introduced which enhance the mechanical strength of normally fragile films. Mechanical strength has been imparted to thin film zirconia membranes prepared for oxygen sensors or high-temperature oxygen-air fuel cells with a technique termed electrochemical CVD (ECCVD) (*33*). The reactants are introduced on either side of a porous alumina membrane and the zirconia grows within the pores to produce a closed-pore, gas tight zirconia membrane only micrometers in thickness.

The principal advantage of CVD is that textured crystal growth takes place during the deposition process. Rapid deposition rates, good composition control, and deposition on surfaces not in the line of sight can be achieved in complex compounds by CVD, although often with the disadvantage of relatively high processing temperatures. This restricts the choice of substrate materials and introduces problems of interdiffusion or of interfacial disturbances between the substrate and the film.

Sol-gel methods. The search for an economical and industrially effective thin film process has recently focused on a technique hitherto developed for the production of high-quality glasses and ceramic powders (*34*). Sol-gel methods involve the preparation of mixed solutions of organometallic compounds, often metal-alkoxides such as titanium propoxide ($Ti[(CH_3)_2CHO]_4$), in a suitable organic solvent (*35, 36*). This solution is hydrolyzed to form a structured solution or gel containing long chain length metal-organic polymers. After the addition of agents designed to adjust the viscosity and surface tension of the solution, it is spin-, dip-, or aerosol-coated onto an appropriate substrate. On drying, the structure of the polymeric chain is such as to hold the metal ions into a spatial relationship close to that required in the final inorganic phase. The form of the polymer can be adjusted by the type of solvent and through parameters such as the *p*H of the solution. An example of the sol-gel polymer cell structure created in the preparation of magnesium aluminate is shown in Fig. 5 (*37*). On firing the film in a furnace or on a hot plate, the organic components are driven off through carbonization and subsequent oxidation to create an inorganic ceramic film. In general after firing, the structure of the ceramic film is amorphous or partly crystallized and a subsequent annealing process is required to develop the structure fully. In the production of bulk ceramic powders, a disadvantage of the sol-gel process is that large quantities of solutions must be handled and filtered. In thin films, the large surface area is an ideal geometry for the efficient removal of organics. Sol-gel methods have been used successfully for a number of complex piezoelectrics such as PZT (*36, 38*), with recent developments emphasizing high-stability precursor solutions that can be coated on surfaces of complex geometry to produce crack-free films up to 20 μm in thickness (*39*). Films are generally fabricated as single layers of up to 3 μm in thickness with thicker layers being made by successive coatings. Although sol-gel retains the disadvantage with respect to CVD that the primary crystallization is not complete during the initial firing, it is often an appropriate compromise for economy and processing speed. It also provides an effective method for evaluating new compounds and new formulations for materials for device purposes.

Applications of Thin Film Ceramics

A distinction may be made between applications that are essentially passive and those that use the unique functional properties of ferroelectrics and piezoelectrics to create new devices. In both cases an important factor is the bonding between the substrate and the deposited film. With the exception of materials such as zinc oxide which can be deposited at ambient temperatures (*40*), the substrate temperatures ≥600°C necessary for the production of fully crystallized oxide films introduces considerable thermal stress in the film. An important area of research is the development of methods to process films at lower temperatures by means of lasers or high-intensity lamps for rapid thermal firing and annealing. Accommodation of effects arising from thermal expansion mismatch between the film and the substrate can be made by using appropriate buffer layers (*22*). These effects are of particular importance for the deposition of complex oxide layers on silicon or on metallized silicon and metals, and extensive studies are in progress to quantify and understand the requirements to optimize interfacial bonding.

Applications for both passive and active films exist. Along with TiN and SiC, passive alumina layers have been of interest for wear purposes. Sol-gel methods can conveniently deposit such films. Sputtered alumina, yttria (Y_2O_3), and silicon dioxide and monoxide (SiO_2 or SiO) are used in a variety of thin film devices including conventional semiconductor integrated circuits and in the ac-driven thin film electroluminescent displays which were illustrated in Fig. 2. The promise inherent in the development of new types of oxide and ferroelectric films can be illustrated with these devices. In operation, an alternating voltage is applied across a zinc sulfide luminescent material sandwiched between two insulators (*19*). The purpose of the insulators is to limit and control the dc current through the device. The highest efficiency is achieved if the ac voltage drop across the insulators is as small as possible so that virtually all the applied voltage appears across the active luminescent layer. Suitable insulators must have a high transparency, high breakdown strength, and a large permittivity. Lanthanum-doped PZT films offer all of these properties and its use could reduce the operating voltages of electroluminescent displays substantially (*41*).

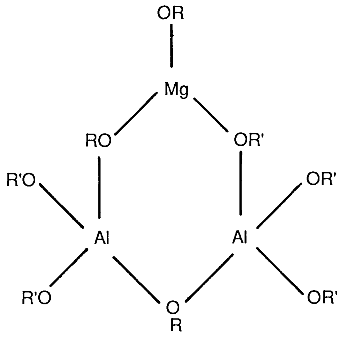

Fig. 5. The atomic placement within a metal-organic polymer formed during the sol-gel processing of magnesium aluminate (*37*). R is an alkoxide radical of the form $[OC_3H_7]$.

A unique opportunity for thin film zirconia exists with the advent of high-temperature superconductors. The reactivity of $YBa_2Cu_3O_{7-\delta}$ with most common substrates is so high that superconductivity is often destroyed in films prepared on all substrates other than single crystal MgO, $SrTiO_3$, or partially stabilized zirconia (*42*). These substrates are impractical for large-scale technical application. Nonreactive zirconia buffer coatings fabricated by a sol-gel process on alumina ceramics or on metal foils would fulfill a currently pressing need. Such zirconia films may also be of interest as nonporous biologically inactive coatings for powders, membranes, and active components to be used in vivo (*18*).

Yttria-stabilized zirconia is an important oxygen ion conducting membrane for potentiometric oxygen concentration cells (*44*) or for high-temperature fuel cells (*45*). If different partial pressures of oxygen P_1 and P_2 are maintained across the membrane, an emf ϵ is developed at temperature T given by the Nernst equation.

$$\epsilon = (RT/4F)[\ln(P_1/P_2)] \qquad (2)$$

where F is the Faraday and R the gas constant. Bulk zirconia cells based on this principle are an important control element in automotive fuel-ignition systems (*3*). The temperature of operation of such cells is limited by the maximum electrical resistance of the zirconia allowed by the electronics. For mechanically strong ceramic this requires a zirconia thickness of about 1 mm and a consequent operating temperature of >600°C. This temperature could be substantially reduced in the potentiometric thin film gas sensors shown in Fig. 6. These employ a ceramic film of the order of microns in thickness in either a planar (bottom), or a coaxial (top) geometry, and use the oxygen equilibrium pressure within a Ni/NiO layer to establish a reference oxygen partial pressure. In principle, sol-gel thin-film technology could provide gas sensors integrated onto silicon or in the form of in-line coaxial sensors which operate at close to room temperature.

The development of high-quality ferroelectric or piezoelectric films provides a wide range of new opportunities in semiconductor

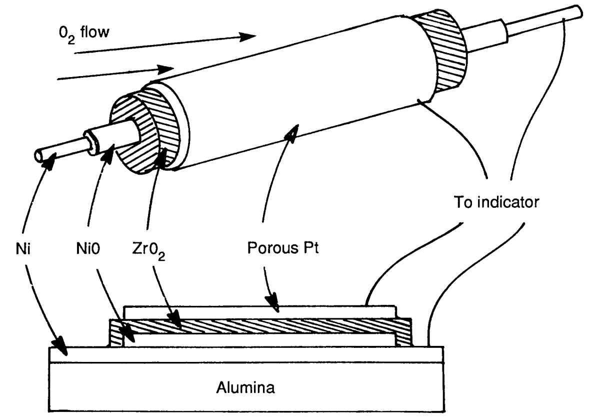

Fig. 6. A thin film oxygen sensor for operation, in principle, in the temperature range 100° to 300°C. The sensor uses a sol-gel zirconia membrane and a Ni/NiO layer structure as an oxygen reference. (**Top**) Coaxial configuration. (**Bottom**) Planar configuration.

devices or ultrasonic devices for medical and engineering applications. The PZT family has the highest piezoelectric coupling constant known, with significant ranges of ferroelectric polarization, dielectric constant, and electrooptic activity which are accessible through impurity doping of the base material (*47*). Initial interest in PZT films was to generate surface and bulk acoustic waves on nonpiezoelectric substrates (*48*). An ac signal applied to a system of interdigital electrodes induces a propagating surface wave that can be detected at a comparable electrode after a time delay set by the surface wave velocity. Since time can be measured with great accuracy, sensitive gas sensors capable of detecting gas concentrations at the level of parts per billion have been developed by measuring the change in surface wave velocity induced by loading the surface by the selective absorption of gas in an organic membrane covering the region between the electrodes (*49*). Sol-gel PZT has been used to coat complex surfaces such as thin metallic wires and optical fibers (*50*) and machined steel surfaces for focused sources for acoustic microscopy (*51*). Coaxial ultrasonic transducers and pressure sensors of extremely small dimensions for medical and biological sensing are possible, while external modulation of light within an optical fiber through the action of ultrasonic stresses set up by an electrically driven coaxial PZT element has been demonstrated (*50*).

The current interest in the semiconductor industry is in the development of solid-state ferroelectric nonvolatile memories (*14*). This technology creates a new set of requirements on the operational capabilities of thin film PZT. The state of the memory is changed by reversal of the ferroelectric polarization in the film, passing once around the ferroelectric hysteresis loop each cycle. The number of cycles during a device lifetime is required to be $>10^{12}$. Ferroelectric "aging," in which the polarization decreases and the coercive forces increase over this lifetime, now becomes an important factor. The studies required to achieve this goal are likely to provide substantial insights into the mechanisms of ferroelectric hysteresis (*15*).

Conclusions

The drive toward miniaturization and circuit integration has been a powerful factor in the development of deposition techniques for thin films of electronic ceramics. The level of technology has now proceeded to where material reproducibility is such that novel elements can be introduced into circuit design and it appears that a range of new circuits, sensors, and applications will enter commercial practice.

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