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Use of sol-gels in the application of ceramic oxide thin films

Bradley Alan Paulson

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Use of sol-gels in the application of ceramic oxide thin films

Paulson, Bradley Alan, Ph.D.
Iowa State University, 1987
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Use of sol-gels in the application of ceramic oxide thin films

by

Bradley Alan Paulson

A Dissertation Submitted to the Graduate Faculty in Partial Fulfillment of the Requirements for the Degree of DOCTOR OF PHILOSOPHY

Major: Chemical Engineering

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Iowa State University
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1987
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DEDICATION

This work is dedicated to the author's wife, Tamra Paulson, sons, Benjamin and Nicholas Paulson, and parents, Carlton and Phyllis Paulson, who have been constant sources of encouragement, support, and enthusiasm.
INTRODUCTION

The development of solid-state electronic circuits, following the invention of the transistor in 1947, opened an entirely new era in the electronics industry. The subsequent miniaturization of such circuits — to the point where the field is now called microelectronics — led to the creation of products that would never have been feasible or affordable in earlier days. These integrated circuits, etched on multiple layers of thin films (0.1 to 10 μm thick), are as remarkable for our ability to manufacture them as they are for the myriad of uses which they have found.

To the general public, some of the results of this change can be seen in the small size of today's radios, in the widespread use of computers in banking and other areas of commerce, and in the availability of personal computers, video cassette recorders, and digital disc players. To those who are more technically trained, the increase in speed and storage capacity of large-scale computers, with a simultaneous decrease in size and in cost per computing operation, is also evidence of this change.

The use of thin-films for constructing integrated circuits has made it possible to reduce weight and to save space by eliminating the need for discrete components. It has also spurred the development of thin-film technology, since the ability to prepare better films at lower cost, and to make films from a greater variety of materials is needed...
(13). In the work described here, an alternative to the customary approach of making thin films by vapor-phase deposition is explored. The procedure is a solution technique called the "sol-gel" process.

The sol-gel process was developed originally at the British Atomic Energy Research Establishment (AERE) at Harwell, England in the early sixties. It has been studied as a means of making protective films for heat engine materials (28), for the preparation of microspheres (500 - 1000 µm in diameter) for uranium carbide fuels for nuclear reactors (85), and for making catalysts and catalyst supports (12,26) and anti-reflective coatings (2). The area where sol-gel methods have been studied most intensively in recent years is the preparation of powders for making high-performance ceramic materials. This will be covered in greater detail in a later section.

Although it has been the subject of many research papers, commercial applications of the process have not been reported in the open literature, except for making glass coatings. It is possible -- even probable -- however, that the process may be in use in certain proprietary manufacturing operations.

Most of the papers describing the use of the sol-gel method for thin film preparation are concerned with silica (SiO_2) films. A few have described the preparation of other simple oxide films such as TiO_2 (5), Al_2O_3 (14), and Ta_2O_5 (36). Still fewer are available on the preparation of mixed-oxide or double oxide films, yet these are the types of film that are of great use in the microelectronics industry. Films of indium-tin-oxide (1), lead zirconate titanate (31), and barium
titanate (16) have been reported.

The present work is concerned primarily with using sol-gel techniques to prepare films of various compounds of the families of the barium titanates, the lithium niobates, and the lithium tantalates. As mentioned earlier, BaTiO$_3$ films have been made by Dosch (16) using the sol-gel method. No reports of films of other members of the barium titanate family, prepared by any method, could be found. Films of LiNbO$_3$ and LiTaO$_3$ have been made by rf sputtering, but no reports of films of other lithium niobates or lithium tantalates could be found. Because precursors of a number of simple oxide films were prepared during the course of this work, films of Ta$_2$O$_5$, Nb$_2$O$_5$, TiO$_2$, Y$_2$O$_3$, and ZrO$_2$ were also made. Of this list of simple oxide films, only those of Ta$_2$O$_5$ and TiO$_2$ have been reported previously as having been made by sol-gel methods.

It should also be mentioned that sol-gel methods may be useful in preparing films of the very new superconducting oxides, such as those of the Y-Ba-Cu-O family.

The barium titanates, the lithium niobates, and the lithium tantalates are ferroelectric materials; that is, upon cooling through their Curie temperatures, electrical domains spontaneously align through mutual interaction, creating highly dielectric materials. The Curie temperatures for barium titanate (BaTiO$_3$), lithium niobate (LiNbO$_3$), and lithium tantalate (LiTaO$_3$) are approximately 125, 1210, and 660°C respectively. Barium titanate, in particular, has a large dielectric constant, of the order of 300 along the c-axis and 5,000 along the
a-axis; consequently, this material is useful in producing capacitors, microwave resonators, computer storage devices, and band-pass filters (6). All three materials are also piezoelectric; that is, a potential difference is produced upon compression, and vice versa, making them valuable materials for electrical-mechanical transducers (6,20,38).

Lithium niobate and lithium tantalate exhibit non-isotropic thermal expansion; expansion along the c-axis is seven times greater than along the a- and b-axes. Upon heating, a virtually self-imposed piezoelectric effect is created as the unequal expansion produces strain in the crystal — the pyroelectric effect (38). They also possess useful optical properties. Strain changes the index of refraction — the acoustooptic effect. An electric field changes the optical dielectric properties — the electrooptic effect. The crystals are birefringent, splitting incident optic beams into ordinary and extraordinary beams. They also have nonlinear optical coefficients, a property which makes them useful in phase shifters, harmonic generators, optical parametric amplifiers, frequency doublers, transverse light modulators, and optical wave guides (20,38).

The properties of all these compounds are stoichiometry dependent and are affected by changing compositions.

Because the use of thin films is growing rapidly in the field of microelectronics, the ability to prepare thin films of barium titanate, lithium niobate, and lithium tantalate is becoming increasingly important. Currently, barium titanate films are produced by flash evaporation, reactive evaporation, and rf sputtering (3). However, both
evaporation and sputtering must be done in a controlled atmosphere and require a substantial amount of power. Evaporation techniques also can lead to stoichiometric shifts as a result of incomplete evaporation and the production of some free barium, while sputtering can lead to contamination by residual gases (3,18,75). Lithium niobate and lithium tantalate are produced by rf sputtering.

In the sol-gel method for preparing thin films, described later in greater detail, a colloidal suspension of the reactants is spun on an appropriate substrate to obtain a dry film, which is then sintered to obtain the crystalline oxide. The method is, in principle, relatively simple, inexpensive, and reproducible. The small particle sizes (on the order of tens to a few hundreds of Angstroms) of the reactants, when prepared as sols, and their related gels, minimize the temperature required to sinter the films. This reduces undesirable film-substrate interactions during sintering. The small particle sizes also promote homogeneity of the films by providing intimate mixing of the reactants.
The reactant particles in the sols used in sol-gel processing are very small and are in the colloidal size range. Colloidal systems consist of two or more phases and have a very large interfacial area to volume ratio (41); at least one dimension usually ranges from about 10 angstroms to 1 micron (33, 67, 73). These systems display properties not found by either bulk matter or simple, true solutions, and as such, are the continuous link between molecular and solid-state chemistry. As can be seen in Table 1, many colloidal systems occur naturally. The table contains only those systems which are relatively easy to classify, and is not a definitive list.

Table 1. Types of simple colloidal systems

<table>
<thead>
<tr>
<th>Phases</th>
<th>Name</th>
<th>Example</th>
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<tr>
<td>Continuous</td>
<td>Dispersed</td>
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<tr>
<td>gas</td>
<td>liquid</td>
<td>liquid aerosol</td>
</tr>
<tr>
<td>gas</td>
<td>solid</td>
<td>solid aerosol</td>
</tr>
<tr>
<td>liquid</td>
<td>gas</td>
<td>foam</td>
</tr>
<tr>
<td>liquid</td>
<td>liquid</td>
<td>emulsion</td>
</tr>
<tr>
<td>liquid</td>
<td>solid</td>
<td>sol or colloid suspension</td>
</tr>
<tr>
<td>solid</td>
<td>gas</td>
<td>solid foam</td>
</tr>
<tr>
<td>solid</td>
<td>liquid</td>
<td>solid emulsion</td>
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<td>solid</td>
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<td>solid suspension</td>
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Sols

The particular systems of interest in this research are solids dispersed in a liquid — the sol or colloidal suspension. A sol is a thermodynamically unstable suspension of solid particles in a liquid (73). If the particles can be optically resolved, then the dispersion is usually referred to as coarse, and not colloidal (72).

Gold sols, produced by reducing gold salts in solution, are the oldest recorded sols; both Johann Kunckels in 1676 (53) and Macquer in 1774 (68) have been credited with concluding that gold sols were actually suspensions of metallic gold particles too fine to see. Berzelius is credited with producing the first sol by hydrolysis, when he hydrolyzed SiS₂ to obtain silica sols in 1833. Sols, in general, were not studied until the 1840s when the Italian scientist, Francesco Selmi, found solutions that exhibited anomalous behavior:

(a) they scattered light, or opalesced;
(b) dissolved substances precipitated upon the addition of a small amount of a non-reacting salt; and
(c) dissolution and precipitation were not accompanied by changes in temperature or volume.

He called these solutions pseudo-solutions; they later became known as sols (73,76). In the 1860s the English chemist Thomas Graham, generally regarded as the father of colloid science, coined the term colloid, from the Greek root "kollos" meaning glue. Graham noted that colloids (a) scattered light,
(b) exhibited slow particle diffusion in the solution,
(c) exhibited low osmotic pressure,
(d) could undergo dialysis,
(e) were aggregatively unstable, and
(f) could undergo electrophoresis (73).

Although Graham initially believed they were two separate states, I. Borshchov, one of his contemporaries, indicated that colloidal solutions may have a crystalline structure. About the same time, the attention of both Tyndall and Faraday was drawn to the opalescence of colloidal suspensions (76). In 1871, Lord Rayleigh explained the blue of the sky by developing the theory of light scattering by colloidal particles (67). Light scattering is wavelength dependent, with blue light scattered more than red light (53, 66, 67, 70). Thus, the sky, tobacco smoke, and diluted milk are blue, while sun rises and sun sets are yellow and red (66). Furthermore, increased particle size also displaces the color of sols to the red end of the visible light spectrum (70), which means that light scattering can be used to determine the size of the particles in a sol.

It was not until much later, during the 1940s, that the physical chemistry of sols began to be studied extensively (69). At about that time Ferenc Körösy, in Hungary, began using sol-gels to produce glass (62). Current metal oxide sol technology originated around the 1950s, at Oak Ridge National Laboratory, primarily to fulfill the need of the expanding nuclear industry as ceramics were found to replace metal fuel elements (17, 22, 26, 62). Sol-gel technology has since expanded into
other fields of interest.

There are two general methods of sol preparation (17,77,78): dispersion and condensation. Dispersive methods of sol production are of industrial importance; a great deal of effort has gone into the design of ball mills, roll mills, homogenizers, and even "colloid mills" to this end (74). The term "colloid mill" is a misnomer, however, since they, like other mechanical comminution devices, produce a wide particle size distribution and only a portion of the product is of truly colloidal dimensions (73). Condensation reactions are the most common methods of sol production. Reduction reactions are used to form metallic elements and hydrolysis reactions are used to form hydrous oxides (32,78,79). The polymerization of a hydroxide is based on the condensation reaction,

\[ -\text{M-} \text{OH} + \text{HO-} \text{M-} \rightarrow -\text{M-O-M-} + \text{H}_2\text{O}, \]

which is catalyzed by either an acid or a base. Replacing the hydroxyl groups with alkoxy groups (OR) produces the analogous reaction,

\[ -\text{M-OR} + \text{RO-M-} \rightarrow -\text{M-O-M-} + \text{ROH}, \]

where R is an alkyl group (CH₃, C₂H₅, etc.). Electro-ionization of a metal salt solution (by dialysis, for example) can also lead to polymerizing condensation reactions (43,66).

Hydrolysis of alkoxydes in non-aqueous solvents actually involves two competing reactions, which proceed simultaneously and are generally incomplete (88). Initially, a fast hydrolysis reaction takes place,

\[ -\text{M-OR} + \text{H}_2\text{O} \rightarrow -\text{M-OH} + \text{ROH}, \]

followed by the slower condensation reactions (7,34,64,87),
\( -M-OR + HO-M \longrightarrow -M-O-M + ROH, \) and  
\( -M-OH + HO-M \longrightarrow -M-O-M + H_2O. \) (2)

An \( S^2 \) type reaction is the most plausible, with the electronegative oxygen atom attacking the more positive metal atom, releasing either alcohol (as in equation 1) or water (as in equation 2). In general, the ease of replacement of the alkoxy groups increases from tertiary to secondary to primary (8). The resulting metalloxane chain (\(-M-O-M-O-M-\)) forms covalent macromolecules which will form giant coordination polymers with each other (7). The metal alkoxides are very sensitive to moisture and readily undergo hydrolysis, so they must be handled in a dry atmosphere until they are added into the water solution. Once they have hydrolyzed, the system is no longer sensitive to water.

While there is a lack of systematic studies that have been reported, the actual reaction rate and reaction products depend on several interdependent reaction variables: a) the specific species and concentration of metal alkoxide (35,39,49,60,74,77,87); b) the water concentration (39,64,87); c) the specific species and concentration of catalyst (35,60,64,74); d) the specific solvent (35,64,71); e) reaction pH (74); f) degree of mixing (74); and g) reaction temperature (35,74,87). However, some generalizations can be made. The use of acids as catalysts tends to lead to linear polymers (7,9,64), while the use of bases as catalysts tends to lead to more branched polymers (9,11,64). Increasing the water to metal alkoxide ratio also tends to lead to more highly branched polymers (54,60). Furthermore, divalent anions tend to lead more readily to instabilities than do monovalent
anions (70,78,79), and the reaction pH and anion-to-metal ratio are critical in determining the aggregation and stability of the sol (33,43,64). Increasing the reaction temperature increases the reaction rate and drives the reaction further towards completion (60,79).

Sols are very homogeneous, and despite the fact that they are thermodynamically unstable, carefully prepared sols may have shelf lives of several months (32,43,48,65), and may be made highly concentrated (up to 10M) (43). As a solution, sols exhibit homogeneity throughout the suspension; this includes the colloid material, as well as the salts dissolved in the solvent. Even multicomponent systems exhibit this homogeneity, which, consequently, has led to many successful studies in magnetic ceramics (4,22). While simple fluids exhibit short-range repulsive forces, sols are dominated by strong, long-range coulombic interactions (19). This leads to the oriented flocculations of crystallites present in gels (22). In addition, the cations in gels are usually in a maximum coordination environment, which aids in low temperature crystallization (58).

The general feeling is that any sparingly soluble solid can be made into a sol (74), although mono- and divalent metals are too soluble and pentavalent metals are not readily dispersed (17). Indeed, hydrolyzed sols of Cr^{3+} (17), Fe^{3+} (73), Mo^{4+} (71), Ta^{5+} (30), Ti^{4+} (17,58), V^{5+} (17), W^{6+} (32), and Zr^{4+} (17,58) are well documented. Livage and Lemerle (33) indicate that almost all transition metal oxides (except those of Group VIIB) can be obtained as gels, with those to the left of Group VIIB on the periodic table occurring as hydrated oxides in their
highest valence state, and those to the right appearing as colloidal metals (zero valence state) or hydroxides. By utilizing the hydrolysis of metal alkoxide solutions in alcohol, compounds such as the mixed cation sols of $\text{BaTiO}_3$ (16,84), $\text{KNbO}_3$ (84), $\text{KTaO}_3$ (84), and $\text{K(Ta,Nb)O}_3$ (84) have also been produced.

Gels

While liquid colloids are known as sols, colloidal solids with both solid and liquid components in a highly dispersed state are called gels (74). Simply stated, gels are the coagulated form of sols (47); that is, most sols can be desolvated to form gels (70). Gels are the interlacing of two continuous phases (72,79); gels, where a large amount of solvent is mechanically entrapped within the solid network (78), are different from gelatinous precipitates, where the solvent is not included in the solid network (32). The particles are generally not amorphous and form microcrystalline bodies (46,79). These rigid bodies are translucent or transparent (72) and although the liquid may comprise up to 99% of the volume (74), extensive properties of both the solid and the liquid phase are evident (47,72): the bodies are solid and can be cut into shapes, but will flow when subjected to slow deformation. The fact that the gel can be made firm, and cut or cast into shapes, has led to studies in which "monolithic" ceramic bodies have been made by direct sintering of gels. However, a high degree of shrinkage, and also cracking, during sintering present serious problems.

When they are first formed, particles of hydrated oxides of
aluminum, iron, thorium, titanium, and zirconium are in the size range of three to four nanometers (23). Although several theories exist for the gelation behavior, multiple agglomeration seems to be the general mechanism by which it takes place (89). A sufficient concentration of these particles will lead to cross-linking as a three dimensional network is established (23,41,79), with lower concentrations leading to softer gels (79).

An uncontrolled flocculation of particles leads to heterogeneities (79), gelation is a controlled flocculation of crystallites, producing an ordered, even anisotropic, solid (22,74). Experimental evidence indicates that the final structure is very much like a sponge, where a mass of long, intertwined fibrils enmesh the liquid (72,78). Once formed, gels contract to reduce interfacial area. If evaporation is prevented, the gel will contract within the liquid, a phenomenon known as syneresis (47,63); the liquid is a second colloidal solution that is not as concentrated as the original (47).

While the rheological behavior of sols is very similar to that of solutions, that is, Newtonian, gels are non-Newtonian; they exhibit thixotropic behavior, with the viscosity decreasing as the shear increases (53,66,72,76). The rheology change between sol and gel reflects the condensation and growth of the polymer species. Viscous processes dominate during Newtonian flow, while elastic interactions become important during thixotropic flow (59). Shear thinning (thixotropy) is evident due to the break down of the colloids, thereby releasing solvent, and causing alignment of the colloids (53). As the
polymers grow and become a more coordinated three dimensional network, the gel becomes more thixotropic, until the body becomes plastic.

Jello is the most familiar gel, in which the solid network of animal protein comprises only 3% of the volume, the remainder being colored, flavored, and sweetened water. Gels are very common in biological systems, where the fluid allows diffusion of oxygen and nutrients, while the polymer network provides structure (33,69). These familiar gels include the cornea and vitreous humor of the eye, synovial fluid of the joints, and gallstones (24,25). More attention is now being given to inorganic gels in which crystals can be grown. In general, these crystals are more perfect and can be grown to better sizes than those crystals grown by solution evaporation (52), because diffusion rates can be more carefully controlled and convection currents are minimized by the gel structure.
SOL-GEL ROUTE TO METAL OXIDE CERAMICS

In the sol-gel method for making oxide ceramics, concentrated colloidal suspensions (sols) of a hydrous oxide or hydrous hydroxide precursor are dehydrated to form gels which yield an oxide upon calcination (82). Although most of the previous work has been done with glass forming systems (specifically silica and alumina), sol-gel work is now being done with a broader range of metal alkoxides (57). Current work involves producing powders, bulk monolithic parts, fibers, and composites (11). The sol-gel route is relatively simple and is carried out under mild conditions. Thus, it leads to simplification of the production of bulk sintered metal oxide ceramics and broadens the variety of materials that can be produced, particularly mixed-oxide ceramics (85,88).

The sol-gel technique may involve relatively long processing times if slow drying of the gel is necessary. It also requires the use of potentially dangerous solvents, the need for controlled atmospheres during raw material preparation and handling, and the use of expensive raw materials (34). However, it does offer several advantages, as can be seen in Table 2.

Since the preparation of ceramic precursor powders by a sol-gel process is done in a liquid phase, pickup of impurities and production of dust is minimal (17). Furthermore, the use of alkoxides, especially when they are carefully purified, reduces the probability of ionic
impurities and produces organic reaction products which can be easily volatilized (71). When reactants are mixed directly by comminution, or when comminution is used to break up a chemically prepared precipitate, dust is evolved and erosion of the grinding media provides the opportunity for contamination of the powder. These are critical considerations when working with toxic materials or with high purity technical ceramics.

Sol-gel reactions also facilitate the preparation of multicomponent materials; the mixing of sols can provide a high degree of mixing, on a very small scale, of the reactants. This is important in making electronic ceramics. Powders produced by coprecipitation are seldom homogeneous on the microscopic level. Although some complexing seems to occur in solution (55,64), the reaction rates of the mixed alkoxides must be similar in order to obtain particles which are homogeneous on
the microscopic scale (29,86). Fortunately, if the desired oxide is not obtainable by simultaneous hydrolysis, it is possible to obtain a mixed cation sol by blending the sols of two different oxides (23).

As with most precipitation reactions, the particle size and shape are intimately related to the conditions present at the time when the sol is formed, so the reaction can be used to control the particle size and shape (83,87). Sols tend to produce spherical particles with a narrow size distributions as a result of the homogeneity of the suspension. Komarneni and Roy (26) have precipitated titania spheres in an alcoholic hydration polymerization and found that in a solution dilute enough to avoid gelation, the amount of added nitric acid affected the nature of the precipitate. In precipitating molybdenum and cobalt sulfide from sols, Haruta et al. (21) found that the particle sizes (0.08 to 0.4 microns and 0.09 to 0.7 microns, respectively) could be controlled by the pH of the mother liquor.

The small particles in the sols lead to an extraordinary reduction in the temperature required for sintering and the chemical reactions in powders produced by sol-gel methods (22,36). The sintering rate, or rate of densification, is proportional to the diffusion coefficient of the material divided by the cube of the particle radius, $D/r^3$. Thus, at a given temperature (constant $D$), smaller particles sinter more rapidly and if they are efficiently and uniformly packed, a compact will sinter to a given density at a lower temperature. In practice, Onoda and Hench (45) found that a ten-fold reduction in the particle size of alumina powders led to a 200°C reduction in the sintering temperature. Thoria
(melting point 3220°C) of 99% theoretical density has been produced from sol-gel derived material at a sintering temperature of 1150°C (82). By analogy, using the ratio of absolute sintering temperature to absolute melting point as a method of estimating the required sintering temperature, BaTiO$_3$ (melting point 1705°C) and LiTaO$_3$ (melting point 1640°C) could produce dense ceramics at 500°C. This is characteristic of the sol-gel technique for the production of ceramics, consequently making it an attractive method for materials that can not, or should not, be exposed to extreme conditions. It also permits the production of dense ceramics at moderate sintering temperatures, reducing both capital and production costs incurred by sintering at extremely high temperatures.

Recent work has been done to produce bulk ceramics by sintering gels directly as monolithic shapes. This is motivated by the high purity and homogeneity available, the potential of a viscous liquid to minimize defect sources, the ability to visually inspect dry gels, the potential of shaping gels, and the lower temperature required to sinter the material to a high density ceramic (14). However, since the gel usually contains a large amount of liquid, a great deal of shrinkage occurs. Different evaporation rates in the bulk gel bodies lead to internal stress which results in cracking of the bodies (60), which, together with the large shrinkage involved, leads to size and shape limitations of the final product (4,14,22).

The cost of sol-gel processing may be prohibitive for the production of powders and the technical problems make sol-gel processing
a difficult method for the production of monolithic bodies. However, for special applications or for the preparation of extremely pure materials, these limitations may be acceptable. Sol-gel processes for the direct production of ceramics appear to be most attractive as a method of preparing films, but even when films are prepared, one can encounter crazing and poor adhesion to the substrate. The thickness of the film, the relative thermal expansion coefficients of film and substrate, and the chemical homogeneity of the dried, unsintered film are important.
FILMS VIA COLLOIDAL INTERMEDIATES

While the sol-gel technique may be too expensive for the routine production of many types of ceramic powders and monoliths, the application of thin films via colloidal suspensions should be highly cost effective. There is no need for complicated, costly equipment; the only significant cost is that of the raw materials. Furthermore, as deposition rates and stoichiometries can be difficult to control in alternative methods of film production, the sol-gel route can be very attractive for complex compounds (34).

In using sol-gels to apply films, sols of the desired film composition can be applied by (a) spinning the substrate, producing an even layer of solution, (b) spraying the solution on the substrate, or (c) dipping the substrate in the solution (28,32,40,43). Thus, the method is amenable to placing coatings on complicated shapes (28). The sol film is dried at a controlled rate to form the gel, because rapid solvent loss may cause crazing. The dried film is then heated at moderate temperatures for a relatively short time to form the sintered ceramic coating. Gel coatings usually exhibit extensive densification after sintering at 800°C for approximately 15 minutes, but show significant densification after sintering at even lower temperatures (43). Furthermore, sol-gel derived films exhibit the same merits as do bulk ceramics prepared from sol-gel material:

(a) homogeneous binary or ternary systems can be achieved by mixing
sols (4,40,82);
(b) better crystal size and perfection (4,52,82);
(c) low sintering temperatures -- this reduces the likelihood of thermal distortion and structural damage, as well as film-substrate interaction and temperature gradients within the film (28,40,43,61,82); and
(d) controllable porosity (40,43,82).

Since the physical properties of the sol-gel determine the final film properties, the film characteristics can be controlled by controlling the properties of the sol (27). Films generally range from 0.1 to 2 microns thick (43) and, together with the film porosity, the thickness is dependent upon
(a) reagent concentrations (37),
(b) use of additives (43),
(c) solution rheology (40,43),
(d) state of colloid aggregation (43),
(e) withdrawal rate or spinning speed of substrate (37), and
(f) number of withdrawals or layers deposited (37).

More concentrated solutions produce thicker films with a smooth surface in a shorter amount of time (49). Aggregated sols produce porous coatings (43). Slower velocity of withdrawal produces the most uniform coating when the dip method is used (37). In experiments with silica sols, the optimum "spinnability" occurs when the flow is nearly thixotropic (59).

Schroeder (65) presumed that all metal oxides which are stable in
air may be formed in thin films. Indeed, Perakh and Ginsburg (49) deposited thin films from colloidal suspensions of HgS, Bertrand and Fleischer (5) applied films of TiO$_2$ 800 to 2000 Å thick on GaAs, Perthuis et al. (50) applied "pastes" of both Na$_3$Zr$_2$Si$_2$P$_4$O$_{12}$ and AgZr$_2$(PO$_4$)$_3$ gels, and Nayak et al. (42) applied 100 to 2500 Å thick films of Bi$_{2-x}$Sb$_x$S$_3$ for a distribution of x from zero through two, illustrating the wide range of materials which are amenable to this process.

As was noted in the development of ceramic powders by sol-gel methods, a great deal of work has been done in glass forming systems (12,65,81). In fact, glass companies have been using sol-gel techniques to apply thin films on glass for over thirty years (47,80), with a renewed interest lately in antireflective films (1,2,10,34). With the advances in microelectronics, more work is now being done on semiconducting films. The films of V$_2$O$_5$ made by MacKenzie (34) were obtained by dipping the substrate in the sol or by painting the sol on the substrate (32,33). They were found to have higher conductivities than either crystal or vapor deposited amorphous films (34). Sakka et al. (61) produced sols of BaTiO$_3$ by mixing the isopropoxides of barium and titanium in isopropanol and hydrolyzing the mixture in the presence of acetic acid. Films 0.05 to 0.25 microns thick were obtained by dipping stainless steel substrates in the sol and sintering at 500°C for ten minutes. The sol-gel produced BaTiO$_3$ films of Dosch (16), which were made by hydrolyzing titanium isopropoxide in a methanolic solution of barium hydroxide, were calcined at temperatures from 100 to 900°C.
Wu et al. (84) produced sols of BaTiO$_3$, KNbO$_3$, and KTaO$_3$ by refluxing the alkoxides in methanol and letting the solutions slowly hydrolyze in air. They found that methanol was necessary as the solvent to prevent precipitation during hydrolysis. Films were applied to substrates, crystallized at temperatures from 550 to 700°C, and subsequently sintered at temperatures from 1100° to 1350°C.
EXPERIMENTATION

In concept, the sol-gel route to producing thin films is quite simple and straightforward. No customized techniques or equipment are required, organic solvents can usually be found in which both water and the metal alkoxide are soluble and the sols are easily mixed in desired reactant ratios (15). Experience has also shown that the molar ratios of the metal species in the starting sols are maintained in the film. It should be possible to make a film of any oxide for which a sol-gel of the precursor material or materials can be made. However, the crucial point is that the precursors of the materials of interest must be made as sols, and then converted to a gel. Further, the sols must be stable long enough to permit the film to be applied.

In making alkoxide derived sols, several inter-related factors come into play. The first, and most important, is that the metal alkoxides are extremely water sensitive. If exposed to moist air, they readily hydrolyze, leaving the hydrous metal oxide phase. Thus, all the storage and handling of the alkoxides must be done in a dry box. Filling the dry box with argon simplifies transfer of the alkoxides from the dry box to the open laboratory. The argon, being heavier than air, helps reduce the exposure of the alkoxide to the humidity by inhibiting the mixing of the air into the container holding the alkoxide. Once the alkoxide has been hydrolyzed, producing the desired sol, the mixture is no longer moisture sensitive, and the solvent can be allowed to evaporate into the
In general, stable tantalum oxide sols were easily prepared. However, other alkoxide-derived sols, most notably those made from titanium alkoxide and niobium alkoxide, were much more difficult to make. As stated earlier, obtaining a stable sol of the right concentration involves two competing reactions: hydrolysis and condensation. Hydrolysis is necessary to achieve condensation, but the rate of hydrolysis must be controlled in order to obtain a good sol. Hydrolysis that proceeds too quickly in a given system, relative to the condensation reaction, leads to precipitation of a bulk solid phase rather than a highly dispersed solid phase of colloidal dimensions, while too slow a hydrolysis rate leads to moisture sensitivity in air until the hydrolysis reaction is complete. Thus, the basic problem in obtaining a stable sol is one of regulating the relative rates of hydrolysis and condensation — a kinetics problem.

The reaction variables — system dilution, order of addition, rate of addition, rate of mixing, amount of catalyst, amount of water, and reaction temperature — all affect the rates of the competing hydrolysis and polymerization reactions.

The speed of the condensation reaction has a significant effect on the resulting gel. At high reactant concentrations, even though the hydrolysis reaction is not a problem initially, condensation may proceed so rapidly that pockets of the unhydrolyzed solution are actually trapped within the developing gel network. As the viscosity of the system increases to the point where effective stirring is no longer
possible, the reactants in these isolated pockets of solution tend to hydrolyze as a bulk phase, which becomes "cemented" in the gel matrix. Diluting the reaction mixtures was often the first step in developing a useful sol-gel.

When using the pure alkoxides, as with mixing a methanolic titania sol, it was imperative to add the metal alkoxide to the water mixture. Adding the water mixture to the metal alkoxide left a film of the alkoxide, and subsequently a solid film, on the inside of the reaction vessel. Mixing dilute alkoxides, as in preparing sols with solutions of lithium niobium alkoxide or lithium tantalum alkoxide, was possible in either direction. More dilute solutions allowed for the hydrolysis to proceed slowly no matter which solution was added to the other.

Since the hydrolysis must be controlled, the rate of addition of the pure metal alkoxide into the dilute water solution is also very critical. If it is added too quickly, locally high concentrations are created which lead to locally high hydrolysis rates and the formation of large particles. Since large local concentrations of the metal alkoxide are detrimental to the formation of the homogeneous sol, the stirring rate is critical also. Vigorous stirring which leads to uniform mixing is absolutely essential. This was particularly true of the titanium alkoxide in methanol system. For example, adding the alkoxide to a stagnant volume of a rapidly stirred but poorly mixed solution led to uncontrolled hydrolysis and the formation of bulk solids rather than colloidal particles.

Since it was necessary for all the added impurities to be driven
off during calcination of the film, nitric acid was used as the catalyst in this study, because it breaks down readily upon heating. The amount of catalyst used has a profound effect on the progress of the reaction. A sufficient amount is required to promote condensation, but further addition merely delays gelation. The niobia system was the exception to this; large excesses of nitric acid actually led to bulk precipitation.

Increasing the amount of water usually leads to faster reaction rates, and faster gelation rates. A sufficient excess of water eventually leads to uncontrolled hydrolysis. However, such a simplistic approach is not sufficient to explain why a low water-to-metal concentration in the niobia system led to precipitation; neither does it explain why higher concentrations of water in the titania system produced longer gelation times.

Since controlling the hydrolysis rate was a kinetic problem, the reaction temperature could also affect the results, although all the hydrolysis reactions in the work reported were carried out at ambient temperatures. Reducing the temperature would slow the reactions, allowing for a more orderly hydrolysis.

Temperature was found to have a marked affect when a barium solution was added to a titania sol. As mentioned earlier, the stability of sols are sensitive to the addition of even non-reacting salts. Cooling the hydrated titania sol and the barium alkoxide solution before they were mixed, slowed the destabilization rate of the sol. When this mixing could be accomplished without destabilizing the sol, the mixed cation sol maintained its stability, even after warming.
to ambient temperatures, thus allowing sufficient time for the films to be prepared.

Preparation of Specific Sol-gels

Tantala

Five grams of tantalum ethoxide were added slowly to vigorously stirred solutions of nitric acid and water in methanol, in the amounts shown in Table 3. Except where a precipitate is indicated in the table, all of the sols were stable, but the sol-gel transition occurred at different times as the reaction conditions were altered. The gel formed more slowly as more dilute reaction mixtures were used. This is shown by the longer times required for gelation in the first part of Table 3. The middle part of Table 3 shows that sufficient nitric acid is required to promote the condensation reaction over the precipitation reaction, and that increasing the amount of nitric acid in the system beyond such a point simply delayed the sol-gel transition, probably through enhanced solubility of the tantala polymer. As shown in the bottom part of Table 3, increasing the \( H_2O/Ta \) ratio increased both the rate of hydrolysis and the rate of condensation, but still produced a stable sol until enough water was added to cause uncontrolled hydrolysis. Bulk precipitation, rather than colloid formation then occurred.
Table 3. Tantala gels by condensation hydrolysis in methanol

<table>
<thead>
<tr>
<th></th>
<th>Ta&lt;sup&gt;5+&lt;/sup&gt;</th>
<th>H&lt;sub&gt;2&lt;/sub&gt;O</th>
<th>HNO&lt;sub&gt;3&lt;/sub&gt;</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.62</td>
<td>2.5</td>
<td>0.052</td>
<td>Gel — 5 minutes</td>
</tr>
<tr>
<td>2</td>
<td>0.49</td>
<td>2.5</td>
<td>0.052</td>
<td>Gel — 20 minutes</td>
</tr>
<tr>
<td>4</td>
<td>0.41</td>
<td>2.5</td>
<td>0.052</td>
<td>Gel — 5 hours</td>
</tr>
<tr>
<td>5</td>
<td>0.35</td>
<td>2.5</td>
<td>0.052</td>
<td>Gel — 2 days</td>
</tr>
<tr>
<td>1</td>
<td>0.31</td>
<td>2.5</td>
<td>0.052</td>
<td>Gel — 5 days</td>
</tr>
<tr>
<td>6</td>
<td>0.25</td>
<td>2.5</td>
<td>0.052</td>
<td>Gel — 3 weeks</td>
</tr>
<tr>
<td>7</td>
<td>0.18</td>
<td>2.5</td>
<td>0.052</td>
<td>Gel — month</td>
</tr>
<tr>
<td>8</td>
<td>0.12</td>
<td>2.5</td>
<td>0.052</td>
<td>Gel — 4 months</td>
</tr>
<tr>
<td>15</td>
<td>0.31</td>
<td>2.5</td>
<td>0.0065</td>
<td>Precipitate</td>
</tr>
<tr>
<td>16</td>
<td>0.31</td>
<td>2.5</td>
<td>0.013</td>
<td>Precipitate</td>
</tr>
<tr>
<td>17</td>
<td>0.31</td>
<td>2.5</td>
<td>0.026</td>
<td>Gel — 4 days</td>
</tr>
<tr>
<td>1</td>
<td>0.31</td>
<td>2.5</td>
<td>0.052</td>
<td>Gel — 5 days</td>
</tr>
<tr>
<td>18</td>
<td>0.31</td>
<td>2.5</td>
<td>0.10</td>
<td>Gel — 6 days</td>
</tr>
<tr>
<td>19</td>
<td>0.31</td>
<td>2.5</td>
<td>0.50</td>
<td>Gel — week</td>
</tr>
<tr>
<td>9</td>
<td>0.31</td>
<td>0.62</td>
<td>0.052</td>
<td>Gel — 4 weeks</td>
</tr>
<tr>
<td>10</td>
<td>0.31</td>
<td>1.2</td>
<td>0.052</td>
<td>Gel — 3 weeks</td>
</tr>
<tr>
<td>1</td>
<td>0.31</td>
<td>2.5</td>
<td>0.052</td>
<td>Gel — 5 days</td>
</tr>
<tr>
<td>11</td>
<td>0.31</td>
<td>3.8</td>
<td>0.052</td>
<td>Gel — 8 hours</td>
</tr>
<tr>
<td>12</td>
<td>0.31</td>
<td>5.0</td>
<td>0.052</td>
<td>Gel — 4 hours</td>
</tr>
<tr>
<td>13</td>
<td>0.31</td>
<td>10.0</td>
<td>0.052</td>
<td>Gel — 15 minutes</td>
</tr>
<tr>
<td>14</td>
<td>0.31</td>
<td>20.0</td>
<td>0.052</td>
<td>Precipitate</td>
</tr>
</tbody>
</table>

**Titania**

The production of a methanol-based titania gel was difficult because titanium ethoxide can undergo the ligand exchange reaction,

\[
\text{Ti(OEt)}_4 + 4\text{MeOH} \rightarrow 4\text{EtOH} + \text{Ti(OMe)}_4,
\]

with methanol. If this reaction occurs, the titanium methoxide precipitates out of solution and the desired hydrolysis-condensation reactions cannot take place. Thus, due to the speed of the exchange
Table 4. Titania gels by condensation hydrolysis in methanol

<table>
<thead>
<tr>
<th>Molar Ratios</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti&lt;sup&gt;4+&lt;/sup&gt; (mMole/ml MeOH)</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;O</td>
</tr>
<tr>
<td>#</td>
<td>Ti</td>
</tr>
<tr>
<td>2</td>
<td>0.63</td>
</tr>
<tr>
<td>3</td>
<td>0.55</td>
</tr>
<tr>
<td>4</td>
<td>0.44</td>
</tr>
<tr>
<td>5</td>
<td>0.31</td>
</tr>
<tr>
<td>16</td>
<td>0.15</td>
</tr>
<tr>
<td>17</td>
<td>0.11</td>
</tr>
<tr>
<td>9</td>
<td>0.44</td>
</tr>
<tr>
<td>12</td>
<td>0.44</td>
</tr>
<tr>
<td>13</td>
<td>0.44</td>
</tr>
<tr>
<td>1</td>
<td>0.44</td>
</tr>
<tr>
<td>10</td>
<td>0.44</td>
</tr>
<tr>
<td>11</td>
<td>0.44</td>
</tr>
<tr>
<td>6</td>
<td>0.44</td>
</tr>
<tr>
<td>1</td>
<td>0.44</td>
</tr>
<tr>
<td>8</td>
<td>0.44</td>
</tr>
<tr>
<td>7</td>
<td>0.44</td>
</tr>
</tbody>
</table>

reaction, it is necessary to stir the reaction mixture vigorously in order to avoid the formation of a precipitate. Five grams of titanium ethoxide were added slowly to vigorously stirred solutions of nitric acid and water in methanol. Diluting the reaction mixture slowed the time at which the sol-gel transition took place, as shown in Table 4. Again, sufficient catalyst was required to promote the condensation reaction over the precipitation reaction. Increasing the amount of nitric acid in the system beyond such a point delayed the gelation time, probably through enhanced solubility of the titania polymer.
Furthermore, while the system with an $H_2O/Ti$ ratio of three initially had a higher viscosity than did the systems with ratios of one and two, it actually had a longer gelation time. No specific reason could be found for this apparently anomalous behavior.

**Niobia**

Five grams of niobium ethoxide were added slowly to vigorously stirred solutions of nitric acid and water in methanol. As shown in Table 5, compared to the reactions involving both $Ti(OEt)_4$ and $Ta(OEt)_5$, approximately ten times more nitric acid was required to promote the condensation reaction over the precipitation reaction, even though the exchange reaction of niobium ethoxide and methanol does not lead to precipitation as it does for titanium ethoxide and methanol. Increasing the $H_2O/Nb$ ratio led to more rapid gelation until at high ratios, the uncontrolled hydrolysis reaction caused precipitation.

**Zirconia**

Since zirconium is in the same group as titanium (IV B), it was reasonable to assume that hydrolysis conditions similar to those of titanium would yield zirconium sol-gels of a similar nature. Because it could be produced at moderate reaction conditions and had a reasonably long time for gelation to occur, the titanium sol-gel #1 in Table 4 was used as a reference. Five grams of zirconium n-propoxide, which was available commercially, were added slowly to a vigorously stirred solution of 30 $\mu l$ $HNO_3$ ($HNO_3/Zr = 0.029$) and 540 $\mu l$ $H_2O$ ($H_2O/Zr = 2.0$)
Table 5. Niobia gels by condensation hydrolysis in methanol

<table>
<thead>
<tr>
<th>Nb(^{5+})</th>
<th>Molar Ratios</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>(mmoles/ml MeOH)</td>
<td>H(_2)O Nb</td>
<td>HNO(_3) Nb</td>
</tr>
<tr>
<td>7</td>
<td>0.45</td>
<td>2.5</td>
</tr>
<tr>
<td>8</td>
<td>0.39</td>
<td>2.5</td>
</tr>
<tr>
<td>1</td>
<td>0.31</td>
<td>2.5</td>
</tr>
<tr>
<td>9</td>
<td>0.22</td>
<td>2.5</td>
</tr>
<tr>
<td>10</td>
<td>0.16</td>
<td>2.5</td>
</tr>
<tr>
<td>6</td>
<td>0.31</td>
<td>2.5</td>
</tr>
<tr>
<td>5</td>
<td>0.31</td>
<td>2.5</td>
</tr>
<tr>
<td>4</td>
<td>0.31</td>
<td>2.5</td>
</tr>
<tr>
<td>3</td>
<td>0.31</td>
<td>2.5</td>
</tr>
<tr>
<td>1</td>
<td>0.31</td>
<td>2.5</td>
</tr>
<tr>
<td>2</td>
<td>0.31</td>
<td>2.5</td>
</tr>
<tr>
<td>11</td>
<td>0.31</td>
<td>0.62</td>
</tr>
<tr>
<td>12</td>
<td>0.31</td>
<td>1.2</td>
</tr>
<tr>
<td>1</td>
<td>0.31</td>
<td>2.5</td>
</tr>
<tr>
<td>13</td>
<td>0.31</td>
<td>3.8</td>
</tr>
<tr>
<td>14</td>
<td>0.31</td>
<td>5.0</td>
</tr>
<tr>
<td>15</td>
<td>0.31</td>
<td>10.0</td>
</tr>
<tr>
<td>16</td>
<td>0.31</td>
<td>20.0</td>
</tr>
</tbody>
</table>

in 35 ml ethanol (Zr/EtOH = 0.44 mmoles/ml). The resulting clear, pale yellow fluid gelled overnight.

Germania

Germanium is a Group IV A element, so the sols of titanium were again used as a guide in its preparation. Seven and one tenth grams of germanium (IV) ethoxide were added slowly to a vigorously stirred solution of 30 \(\mu\)l of nitric acid (HNO\(_3\)/Ge = 0.017) and 1002 \(\mu\)l of water
(H₂O/Ge = 2.0) in 40 ml of ethanol (Ge/EtOH = 0.70 mmole/ml). A soft, cloudy gel formed immediately after the reactants were mixed.

**Yttria**

Both yttrium methoxide and yttrium isopropoxide were available commercially as solid powders. Dissolving the powders in a suitable solvent would permit the addition of the alkoxide to an acid/water solution following the same procedure used for the titania, tantala, niobia, zirconia, and germania gels. Unfortunately, yttrium methoxide is not soluble in the typical organic solvents. However, yttrium isopropoxide is soluble in 2-methoxy ethanol. Ethanol was used as the reaction solvent, to avoid the precipitating exchange reaction with methanol which would have led to precipitation. Addition of 1.0 g of yttrium isopropoxide in 10 ml of 2-methoxy ethanol and 10 ml of ethanol to a solution of 5 µl of nitric acid (HNO₃/Y = 0.021) and 100 µl water (H₂O/Y = 1.5) in 30 ml of ethanol (Y/EtOH = 0.13 mmole/ml) produced a clear liquid that gelled in about one week.

**Bismuth Oxide**

Sols of hydrolyzed bismuth were to be produced in much the same way as were the hydrolyzed sols of yttrium. First, a solid bismuth compound was to be dissolved in an appropriate solvent, and then hydrolyzed in the presence of nitric acid; but, alkoxybismuth compounds were not available commercially, so triphenylbismuth was used. The production of BiH₃ is slightly favored thermodynamically over the production of Bi₂O₃.
when triphenylbismuth is hydrolyzed. However, a gaseous product (BiH$_3$) was not evolved during hydrolysis, so it must be assumed that the solid oxide is the kinetically favored product. Furthermore, since the system was to be mixed with a germania sol, which can be made in ethanol, the bismuth sol was also produced in ethanol. Using reaction conditions typical of those for the yttria sols yielded white precipitates. It was necessary to increase the reaction volume and the amount of nitric acid present in the system. Two grams of triphenylbismuth in 10 ml of 2-methoxyethanol were added slowly to a vigorously stirred solution of 70 μl nitric acid (HNO$_3$/Bi = 0.25) and 100 μl water (H$_2$O/Bi = 3.0) in 30 ml ethanol. A crystal clear liquid was obtained from which a gelatinous mass settled out in about a week.

Film Preparation Procedures

Mixed Cation Sols

When mixed cation films are needed, mixed cationic sols can be produced either by first preparing sols of each component and then mixing the two sols, or by mixing the two alkoxide solutions and then hydrolyzing the mixture. Since each alkoxide has its own hydrolysis rate, hydrolyzing the mixed alkoxide solution may lead to microscopic heterogeneities (29,86).

If only one of the components will form a sol, then the use of the sol-gel method for preparing films may still be possible by adding the
second component as a soluble salt. This was the case when lithium niobate, lithium tantalate, and barium titanate films were made, since neither lithium nor barium salts can form sols because of their solubility. However, the addition of even non-reacting soluble substances to a sol can lead to the destabilizing of the sol and the consequent precipitation. It may also be important when the soluble compound is added — before or after hydrolysis of the sol-producing alkoxide.

LiTaO₃ Addition of a lithium nitrate, lithium acetate, or a lithium methoxide solution to a hydrolyzed tantala sol always led to destabilization of the sol and subsequent precipitation. The precipitation could be delayed by using an ice bath to cool the sol, slowing the rate of destabilization to the point where a stable sol would exist for about two days. However, very stable tantala suspensions containing dissolved lithium methoxide could be made by first adding the lithium methoxide to a tantalum ethoxide solution and then carrying out the hydrolysis by adding a solution containing nitric acid and water in methanol. The resulting sols were crystal clear and stable almost indefinitely. Altering the lithium methoxide to tantalum ethoxide ratio in the solution produced the desired stoichiometries for analysis, although increasing lithium content did lead to a reduction in the shelf life of the sol.

BaTiO₃ The sols used to prepare the barium titanate films behaved in exactly the opposite fashion to those used for making lithium tantalate films. In this case the solution of the barium compound had
to be added to the titanium alkoxide solution after the titanium alkoxide had been hydrolyzed. Barium isopropoxide and titanium ethoxide were used for this system. Methanol was used as the solvent. When the barium isopropoxide solution was added to the titania sol, the sol had to be cooled in an ice bath to prevent the destabilizing effect of the barium addition. However, after the mixing had been completed, the sols were stable indefinitely, even after warming to ambient temperatures.

\[ \text{LiNbO}_3 \] As with lithium tantalate, the addition of a solution containing a dissolved lithium salt to the hydrolyzed niobium sol led to destabilization of the sol and subsequent precipitation. The precipitation could again be delayed by using an ice bath to cool the sol and slow the destabilization. However, stable lithium niobate sols were obtained by mixing a solution of lithium methoxide and niobium ethoxide in methanol with a solution containing nitric acid and water in methanol and then carrying out the hydrolysis reaction. The resulting sols were crystal clear and stable indefinitely. Altering the lithium methoxide to niobium ethoxide ratio in solution produced the desired stoichiometries for analysis. Again, increasing the Li/Nb ratio decreased the shelf life of the sol.

\[ \text{Bi}_{12}\text{GeO}_{20} \] Since the germanium actually comprised a very small portion of the reacting material, it was assumed that even with different metal reactivities, mixing the two reactants first and then hydrolyzing them would be superior to mixing the already hydrolyzed sols. Since the germanium is such a minor constituent, the reaction conditions used were the same as those which were favored for the
formation of the bismuth sol. A solution of 25.0 grams triphenylbismuth and 1.20 grams germanium ethoxide (Bi/Ge = 12) in 125 ml 2-methoxyethanol was added to a vigorously stirred solution of 992 μl nitric acid (HNO₃/Bi = 0.25) and 1374 μl water (3 H₂O/2 Bi + 4 H₂O/2 Ge) in 375 ml ethanol. The slightly turbid suspension which resulted was stable for several days before a gelatinous mass began to settle out.

Film application

First, the viscosities of the single component sols were measured in a HAAKE concentric cylinder viscometer. All of the films prepared in this work were spun on silicon wafers. The silicon wafer was stripped of the ever-present layer of silicon dioxide by washing it in a Petri dish containing buffered hydrofluoric acid. It was then washed successively in de-ionized water, acetone, and methanol, and placed on the vacuum chuck of a Headway Research photo-resist spin coating apparatus. Thin films were made by applying 3/4 ml of the suspension to the center of a silicon wafer spinning at 3,000 rpm. As the solvent evaporated from the sol on the spinning substrate, the sol became more and more concentrated, causing the formation of a gel. A short time later the gel would dry even further, producing a film. A dry film was usually produced in about 30 seconds. A second layer was applied to the top of the first, dry film to reduce the likelihood of pinholes. Thick films for x-ray analysis were obtained by applying successive layers on the silicon wafer.
Calcination

After the dried films were obtained, they were sintered to produce the crystalline, coherent ceramic film. This was done by placing the wafers in quartz boats and heating them in Blue M muffle furnaces. The wafers were heated up to 700°C at the maximum furnace heating rate and held there for one hour, at which time the furnace was turned off. The wafers were cooled for a half hour in the open furnace and then for another half hour on the open furnace door. They were then removed from the quartz boat and placed in Petri dishes.

Film Characterization

The sintered wafers were examined visually for crazing, cracks, and macroscopic heterogeneities. They were then examined in greater detail in a scanning electron microscope before physical and electrical measurements were made.

Profilometer

In the absence of interference methods of determining film thicknesses, such as ellipsometry, the silicon wafers were cleaved, placed on edge, sputtered with gold, and the cross sections were observed with a scanning electron microscope (SEM). However, the integrity of the ceramic film edge could not be maintained, even after mounting the wafer in mounting media, prohibiting the measurement of the film thickness. Thus, bands of polisher's mounting pitch were placed across the surface of the single component ceramic films, and after
drying, the wafers were placed in hydrofluoric acid to etch away the exposed film. Once the film was removed from the wafer, the wafer was washed with deionized water to arrest the etching of the silicon. After removing the pitch with 1,1,1 trichloroethane, the wafers were washed with acetone and dried. The film thickness was then measured with a Tencor Instruments Alpha-step profilometer. In this mechanical technique, the vertical displacement of a diamond shaped needle is measured by a transducer and the signal is amplified and recorded on a strip chart recorder. The profile of the film is reproduced with high accuracy, but the system is sensitive to variations in the surface, both that of the etched wafer and the film.

Composition

Several techniques are recommended for the analysis of thin films, including electron diffraction, x-ray diffraction, and electron microscopy, to identify the structure of thin films, and emission dispersive analysis, Auger electron spectroscopy, and electron microprobe, to identify the elemental composition of the films. Since a small angle reduces the contributions of the substrate, the technique of choice for the analysis of thin films is small angle x-ray diffraction. However, this type of equipment was not available, so the films were analyzed using Auger electron spectroscopy, emission dispersive spectroscopy, and x-ray diffraction.

**Auger Electron Spectroscopy** One of the barium titanate films was analyzed by Auger electron spectroscopy (AES). A hole was sputtered
through the film to the surface of the silicon wafer and the elemental composition of the film was determined as a function of the distance into the film.

**Emission Dispersive Spectroscopy**  
In emission dispersive spectroscopy (EDS), an x-ray beam passes into the surface of the sample and the dispersed radiation, upon analysis, yields the semi-quantitative elemental composition of the sample. Since the films are relatively thin, the beam can pass through the film and into the silicon substrate. Thus, the amount of silicon analyzed can be used as an index of the relative film thickness. Thinner films allow the x-rays to penetrate more deeply into the silicon wafer, leading to a greater content of silicon in the analytical results; thicker films show a lower silicon content. None of the samples gave any significant variation in silicon composition concentration across the surface of the sample, showing that the films were uniform in thickness across the wafer.

**X-ray Diffraction**  
While a Ba/Ti ratio can be determined approximately by EDS, EDS can not differentiate between a stoichiometric compound, such as BaTiO₃, and a mixture of the constituent oxides, i.e., BaO and TiO₂. However, x-ray diffraction (XRD) can identify the phase present in a sample. The x-rays pass through the film and into the silicon wafer. Thus, the diffraction pattern of the film will be superimposed upon the pattern of the silicon wafer. The intensity of the pattern of the film can be amplified by cropping the very intense peak of the silicon wafer in the observed diffraction pattern. Increasing the sintering temperature increases the amount of
crystallinity in the film. Increasing the thickness of the film, by increasing the number of layers placed on the substrate, increases the amount of material available to produce an x-ray pattern.

Capacitance

Thin film capacitors were produced for the determination of the dielectric constants by evaporating aluminum on the film surface, coating the aluminum with photo-resist, and patterning the photo-resist into 5mm squares. The aluminum was etched off the area surrounding the squares with a phosphoric acid-acetic acid-nitric acid etchant (PAN etch). Leads were attached to the aluminum squares and to the aluminized wafer back and the ceramic film capacitance was measured using an AC bridge circuit. The dielectric constant of the ceramic could then be calculated using the equation

\[ C = \frac{\varepsilon_0 \varepsilon_r A}{d}, \]

where

- \( C \) = film capacitance, in Farads,
- \( \varepsilon_0 \) = permittivity of free space = \( 8.854 \times 10^{-12} \) F/m,
- \( \varepsilon_r \) = film dielectric constant,
- \( A \) = capacitor area, in square meters = \( 2.5 \times 10^{-5} \) m\(^2\), and
- \( d \) = film thickness, in meters.
RESULTS

The sintered films on the silicon wafers displayed coloring as a result of reflective optical interference, which was dependent on the index of refraction and thickness of the film. This phenomenon combined with certain imperfections such as flowering in the center of some of the wafers, which was the result of the rapid acceleration to the final spinning speed following the application of the sol-gel, produced spectacular visual effects. Some wafers also exhibited radial striations, a result of the film drying too quickly during the spinning operation. Surface occlusions, a result of dust adsorption on the film surface, were also present. These flaws, which can be eliminated by careful control of sol viscosity and spinning conditions, and by preparing the films under clean-room conditions, were not considered to be detrimental to the quality of the films. On most of the films there were large smooth areas that could be examined in detail and could be used to measure the properties of the films.

Under the optical microscope, the films were smooth and coherent in appearance. There was no detailed grain structure, and the films exhibited no activity in polarized light. Except for the striations and dust occlusions, the films looked very homogeneous. Even under the scanning electron microscope (SEM), the films showed no discernible detail.

Very viscous sols tended to dry so rapidly that a smooth radial
flow over the surface of the wafer could not be achieved when the film was spun. This caused severe crazing of the film and, in some instances, resulted in a powder being deposited on the wafer, rather than a film.

However, this situation could be avoided by using a less viscous sol. Since the viscosities of the single component sols were measured just prior to spinning, these sols were used to model the application of the film on a spinning substrate. The more viscous sols were more non-Newtonian in their rheological behavior; the effect became pronounced at an apparent, or Newtonian viscosity of about 10 cp. The viscosities recorded for the sols were apparent Newtonian viscosities calculated at a shear rate of 1000 seconds$^{-1}$.

Film Application Model

The application of colloidal films on a spinning substrate has been shown to produce films of uniform thickness on small circular substrates (40). Ling et al. (30) gives the following empirical equation for photo-resist films formed on a spinning substrate,

$$d = K(w)^{-0.5},$$

where

- $d =$ film thickness, in angstroms,
- $K =$ constant combining the characteristics of the spinner and the viscosity of the photo-resist solution, and
- $w =$ spinning speed, in thousand rpm.

Thus, a specific spin coat apparatus and photo-resist solution gave a
straight line with a slope of \( K \) when the film thickness, \( d \), was plotted against the inverse of the square root of the spinning speed, \( w \). When they applied this equation to the spinning of \( \text{Ta}_2\text{O}_5 \) films derived from ethanolic sol-gels, they obtained a value of 1400 for the constant, \( K \).

The use of the photo-resist equation to correlate film thickness with spinning speed for the single oxide sols prepared in the present work gave the results shown in Figure 1. A separate straight line was obtained for each sol. Values for the constant \( K \) ranged from 400 for the 0.9 cp \( \text{TiO}_2 \) sol to 3500 for the 26.2 cp \( \text{TiO}_2 \) sol. In general, increasing the sol viscosity increases the value of \( K \), as would be expected.

Plotting the film thickness as a function of the viscosity, \( \mu \), at constant spinning speed, as shown in Figure 2 for spinning speeds of 1000 rpm, 3000 rpm, 4000 rpm, and 6000 rpm gave straight lines in each case. Neither the specific oxide nor the solvent used appeared to have a significant effect. The linear relation between film thickness and sol viscosity can be expressed

\[
d = m \log(\mu) + b,
\]

where both \( m \) and \( b \) decrease as the spinning speed increases.

Since the equations,

\[
d = K(w)^{-0.5} \quad \text{and} \quad d = m \log(\mu) + b,
\]
describe the thickness of the sintered film at constant \( \mu \) and \( w \), respectively, \( K \) should be a function of \( \log(\mu) \) while \( m \) and \( b \) should be
Figure 1. Effect of the spinning speed during film application on the film thickness

functions of \( (w)^{-0.5} \). Substituting these identities into each equation, produces a single equation,

\[
d = a(w)^{-0.5} \log(\mu) + c(w)^{-0.5}.
\]

Thus, a plot of \( d(w)^{-0.5} \) versus \( \log(\mu) \) should produce a straight line
Figure 2. Effect of the sol-gel viscosity on the film thickness: a) 1000 rpm; b) 3000 rpm; c) 4000 rpm; and d) 6000 rpm

with a slope of $a$ and an intercept of $c$. As shown in Figure 3, the equation,

$$d = (w)^{-0.5}(2000 \log(\mu) + 350),$$

does indeed describe the data. The relationship is independent of the
Figure 3. Dependence of the film thickness on the sol-gel viscosity and the spinning speed during film application.

material, solvent, and concentration. One also should be able to use this equation to estimate the film thickness that will be obtained for other acid-catalyzed oxide sols or for sols whose particles and gel structure are similar to those used to obtain the correlation. Systems
with different structures, such as base-catalyzed oxide sols may fit the equation but the constants might be different. This assumption would have to be tested first, since it is reasonable to assume that different kinds of sol structures will behave differently under shear.

**Film Characterization**

The crystal structure of the films was determined, where possible, by x-ray diffraction. Although a great deal of the pattern from the silicon wafer was picked up during the x-ray diffraction work, it frequently happened, after cropping the silicon peaks, that there was enough activity to determine the structure of the films. The elemental composition of several barium titanate (BaTiO₃) films was examined by emission dispersive spectroscopy, film thickness was measured with a profilometer, and the elemental profile as a function of depth in the film was studied by Auger electron spectroscopy. These measurements, together with capacitance measurements provided an overall view of the quality of the films that had been prepared by the sol-gel method.

**X-ray diffraction analysis**

**Single oxides**  X-ray diffraction patterns were obtained for all of the single oxide films — Nb₂O₅, Ta₂O₅, TiO₂, ZrO₂, and Y₂O₃. Interpretation of the diffraction patterns for these films was easily done. In each case the expected composition of the film was confirmed. Except at extremely high temperatures, yttria exists as only one phase. The other single component oxides could exist as one of several (or a
combination of two or more) phases. However, each material was present as only a single phase, with delta niobia, orthorhombic tantala, anatase titania, and cubic zirconia being those phases.

**Barium titanate** During the film preparation procedure, hydrolyzing the mixed alkoxide solution of barium and titanium led to precipitation, rather than sol formation. However, it was found that a barium alkoxide solution could be added to the hydrolyzed titania sol under the proper conditions, without destabilizing the sol, as explained in the Experimentation section. It remained to be proved that calcining this mixture would, in fact, produce a barium titanate ceramic of the desired composition. A mixed BaO and TiO$_2$ ceramic would exhibit large peaks at two theta ($2\theta$) values of 12 and 14, as shown in the x-ray diffraction standards reproduced in Figure 4 for these materials. However, from the diffraction standards for BaTiO$_3$ shown in Figure 5, it is evident that the peak at $2\theta = 12$ would be absent in the diffraction pattern of a crystalline BaTiO$_3$ film. In order to verify the composition of the sol-gel derived barium-titanium films by x-ray diffraction analysis, it was necessary to spin multiple layers on the silicon substrate. This produced a sufficient amount of material in the film to give a definitive x-ray diffraction pattern. The results for consecutively thicker films are shown in Figure 6. The single layer film was about 500 Å thick.

Silicon is responsible for the alpha peak at $2\theta = 30$, the beta peak at 27, and the half angle peak at 15. The thickest film (3000 Å), that produced by seven layers, was thick enough that the composition of the
Figure 4. X-ray diffraction standards of BaO and TiO$_2$.

Figure 5. X-ray diffraction standard of BaTiO$_3$. 
film to be determined. It exhibited a strong peak at $2\theta = 14$, and minor peaks at 10, 18, 20, and 25, which corresponds to the pattern produced by barium titanate. The major peak at $2\theta = 12$ for titanium dioxide and barium oxide, shown in the standards in Figure 4 for these compounds, is conspicuously absent in Figure 6, indicating that the film is indeed barium titanate ($\text{BaTiO}_3$).

However, $\text{BaTiO}_3$ films have been produced by Dosch (16), Sakka et al. (61), and Wu et al. (84) using the sol-gel method, so the unique advantages of adding the barium alkoxide solution to the hydrolyzed titania sol are not readily apparent. Dosch hydrolyzed a solution of
barium hydroxide and titanium ethoxide to produce a barium titanate compound with a barium to titanium ratio of 1/4. The solution chemistry of this process would permit barium titanate with higher, but not lower, Ba/Ti ratios to be made; titanium methoxide requires two hydroxyl groups for every four titanium atoms in order to form a soluble complex in methanol prior to hydrolysis.

From a commercial point of view, barium titanates with lower Ba/Ti ratios — such as BaTiO$_5$ and Ba$_2$Ti$_9$O$_{20}$ — have better electrical properties, especially at microwave frequencies. This subject is covered in greater detail in the Discussion section. Therefore, the unique advantage of being able to add the barium solution to the hydrolyzed titania sol, without destabilizing it, could only be demonstrated if other barium titanate compounds could be prepared as films. As shown in the x-ray diffraction standard in Figure 7, BaTi$_5$O$_{11}$ exhibits major peaks at 2$\theta$ values of 13 and 14, and minor peaks at 11, 12, 16, 19, 20, and 22. The x-ray diffraction pattern of the film in Figure 8 exhibits these peaks, as well as omitting the major peaks that would be present at 2$\theta = 12$ if a compound of mixed BaO and TiO$_2$ were present. Films of Ba$_2$Ti$_9$O$_{22}$ would exhibit a major peak at 2$\theta = 13$, with minor peaks at 12, 15, 18, 19, and 26, as is seen in the standard x-ray diffraction pattern in Figure 9. However, films of Ba$_2$Ti$_9$O$_{22}$ were not thick enough to give definitive results after XRD analysis. Since the film has the composition of the precursor sol, XRD analysis was done on the powder after gelation, drying, and calcination. Again, as can be seen in Figure 10, the major peak of BaO and TiO$_2$ is
Figure 7. X-ray diffraction standard of BaTi$_5$O$_{11}$

Figure 8. X-ray diffraction pattern of a sol-gel derived BaTi$_5$O$_{11}$ film on silicon
Figure 9. X-ray diffraction standard of $\text{Ba}_2\text{T}_{19}\text{O}_{20}$

Figure 10. X-ray diffraction pattern of a sol-gel derived $\text{Ba}_2\text{T}_{19}\text{O}_{20}$ powder
absent at $2\theta = 12$, while the major peak at 13 and the minor peaks at 12, 14, 18, and 19 are evident, indicating that the film is composed of $\text{Ba}_2\text{Ti}_9\text{O}_{20}$. Furthermore, the existence of peaks at $2\theta = 25$ and 26 indicate that the powder is not composed of $\text{BaTi}_5\text{O}_{11}$. All the films of the mixed barium titanates yielded the barium titanate compound of the desired stoichiometry after calcination. The BaO and TiO$_2$ peaks did not appear in any of the XRD patterns, indicating that the films were the correct barium titanate compounds, and not mixtures of barium oxide and titanium dioxide.

**Lithium niobate and lithium tantalate** Both lithium niobate and lithium tantalate sol-gels had the same character; starting mixtures of the desired stoichiometry could be made by adding the lithium methoxide to the already hydrolyzed niobia or tantala sols, yielding sols with limited stability but which were stable for sufficiently long periods that they could be spun on the silicon substrate. After calcination, the films were a mixture of the desired lithium compound with the heavy metal oxide, which is illustrated by comparing the x-ray diffraction patterns of Ta$_2$O$_5$ and LiTaO$_3$ standards in Figures 11 and 12, respectively, with the pattern of the sol-gel derived film in Figure 13. Again, silicon is responsible for the alpha peak at $2\theta = 30$, the beta peak at 27, and the half angle peak at 15. Strong orthorhombic Ta$_2$O$_5$ peaks can be seen at $2\theta = 10, 13, 17, \text{ and } 25$, with weak peaks at 21 and 25, and the strong lithium tantalate peak at $2\theta = 11$, with minor peaks at 15, 16, 19, 22, 24, and 25. Thus, the film produced by mixing the lithium solution with the already hydrolyzed
Figure 11. X-ray diffraction standard of Ta$_2$O$_5$

Figure 12. X-ray diffraction standard of LiTaO$_3$
Figure 13. X-ray diffraction pattern of a sol-gel derived film made from a mixture of lithium methoxide with a tantala sol. Both \( \text{Ta}_2\text{O}_5 \) and \( \text{LiTaO}_3 \) are present in the calcined film.

tantala sol produced a film which was a mixture of \( \text{LiTaO}_3 \) and \( \text{Ta}_2\text{O}_5 \). Lithium niobate films derived in the same manner gave analogous results. As can be seen in Figure 14, a film of \( \text{Nb}_2\text{O}_5 \) would have major peaks at \( 2\theta = 10 \) and 13, with minor peaks at 16, 21, 23, and 25, while as shown in Figure 15, a lithium niobate film would have a single major peak at 11 and a minor peak at 15. However, as shown in the XRD pattern of the film produced by adding the lithium solution to the hydrolyzed niobia sol in Figure 16, the film has major peaks at \( 2\theta = 10, 11, \) and 13, indicating that it is a mixture of \( \text{Nb}_2\text{O}_5 \) and \( \text{LiNbO}_3 \).

On the other hand, in these two systems, unlike barium-titanium systems, it was possible to mix the lithium alkoxide with either the niobium or the tantalum alkoxide in the desired proportions before
Figure 14. X-ray diffraction standard of Nb$_2$O$_5$

Figure 15. X-ray diffraction standard of LiNbO$_3$
Figure 16. X-ray diffraction pattern of a sol-gel derived film made from a mixture of lithium methoxide with a niobia sol. Both Nb$_2$O$_5$ and LiNbO$_3$ are present in the calcined film.

hydrolysis. Different films were produced when this was done. The films produced by this method contained only the desired lithium niobate or lithium tantalate. No Nb$_2$O$_5$ or Ta$_2$O$_5$ was present. This can be seen in the diffraction pattern for lithium tantalate, where the lithium tantalate diffraction pattern is superimposed on the diffraction pattern of silicon in Figure 17. The major peaks at $2\theta = 10, 13, 17, \text{ and } 25$ for Ta$_2$O$_5$ are absent, indicating that the film is indeed lithium tantalate. The only peak in Figure 18, at $2\theta = 11$, indicates that the film contains no Nb$_2$O$_5$ and is lithium niobate.
Figure 17. X-ray diffraction pattern of sol-gel derived film made from a sol produced by hydrolyzing a mixed solution of lithium and tantalum alkoxides. The film consists only of LiTaO$_3$; no Ta$_2$O$_5$ is present.

Figure 18. X-ray diffraction pattern of sol-gel derived film made from a sol produced by hydrolyzing a mixed solution of lithium and niobium alkoxides. The film consists only of LiNbO$_3$; no Nb$_2$O$_5$ is present.
Capacitance Characterization

Since the barium titanates, lithium niobates, and lithium tantalates are dielectric, and those properties are related to the stoichiometry of the compound, one of the purposes of this work was to observe the trends in the dielectric constant as the compound stoichiometry shifted. Stoichiometric ratios of known compounds were used. The resulting films were characterized by XRD and used to obtain thin film capacitors. In those instances where the sol had a limited shelf life (the lithium tantalate and lithium niobate compounds with high lithium content), the sols were duplicated and duplicate films were obtained to investigate any variations that might have occurred as a result of the limited stability of the sol.

**Barium titanate**

Since the barium titanate films were very stable and experiments indicated that sols of the mixed composition produced ceramics of the desired stoichiometry, no films were duplicated. The dielectric constants of TiO$_2$ and BaTiO$_3$ are reported to range from 14 to 110 and 15 to 30,000. However, as in the case of BaTiO$_3$, in particular, even the best evaporated films seldom reach dielectric constants over 700. Furthermore, Plourde et al. (51) and O'Bryan et al. (44) report values at 4 GHz that have a maximum at about 50 for BaTi$_{5}$O$_{11}$ and decrease to about 40 at BaTi$_{4}$O$_{9}$. Thus, the calculated dielectric constants are in the typical ranges, as seen in Table 6. They also reported a dielectric
Table 6. Barium titanate films produced by sol-gels

<table>
<thead>
<tr>
<th>Mole Ratio</th>
<th>Mole Fraction $X_T$</th>
<th>Compound</th>
<th>Film Capacitance (nF)</th>
<th>Film Thickness (Å)</th>
<th>Dielectric Constant $\varepsilon_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0/1</td>
<td>1/1</td>
<td>TiO$_2$</td>
<td>96</td>
<td>600</td>
<td>26.0</td>
</tr>
<tr>
<td>1/5</td>
<td>5/6</td>
<td>BaTi$_6^{0.11}$</td>
<td>30</td>
<td>875</td>
<td>11.9</td>
</tr>
<tr>
<td>2/9</td>
<td>9/11</td>
<td>Ba$<em>2$Ti$</em>{9.20}$</td>
<td>64</td>
<td>850</td>
<td>24.6</td>
</tr>
<tr>
<td>1/4</td>
<td>4/5</td>
<td>Ba$<em>2$Ti$</em>{7.20}$</td>
<td>45</td>
<td>700</td>
<td>14.2</td>
</tr>
<tr>
<td>4/13</td>
<td>13/17</td>
<td>Ba$<em>4$Ti$</em>{13.30}$</td>
<td>35</td>
<td>1150</td>
<td>18.2</td>
</tr>
<tr>
<td>6/17</td>
<td>17/23</td>
<td>Ba$<em>4$Ti$</em>{10.40}$</td>
<td>24</td>
<td>1150</td>
<td>12.5</td>
</tr>
<tr>
<td>2/5</td>
<td>5/7</td>
<td>Ba$<em>5$Ti$</em>{12.0}$</td>
<td>20</td>
<td>2025</td>
<td>18.3</td>
</tr>
<tr>
<td>1/2</td>
<td>2/3</td>
<td>Ba$<em>5$Ti$</em>{12.0}$</td>
<td>29</td>
<td>1800</td>
<td>23.6</td>
</tr>
<tr>
<td>1/1</td>
<td>1/2</td>
<td>BaTi$_3$</td>
<td>19</td>
<td>2300</td>
<td>19.7</td>
</tr>
<tr>
<td>2/1</td>
<td>1/3</td>
<td>Ba$_2$Ti$_3$</td>
<td>19</td>
<td>2600</td>
<td>22.3</td>
</tr>
</tbody>
</table>

constant minimum at 80 mole percent titanium. While there is a great deal of activity at that point, as seen in the table, no such trend is evident; no significant trends are apparent.

**Lithium tantalate**

The capacitance of four lithium tantalate compounds and of pure tantalum (V) oxide were measured, and the corresponding dielectric constants were calculated. Because of the reduced stability of the sol as the lithium to tantalum ratio increased, films of Li$_3$TaO$_4$ and Li$_7$TaO$_6$ were duplicated. As shown in Table 7, the capacitance, film thickness, and calculated dielectric constants of the duplicated films
Table 7. Lithium tantalate films produced by sol-gels

<table>
<thead>
<tr>
<th>Mole Ratio</th>
<th>Mole Fraction</th>
<th>Compounda</th>
<th>Film Capacitance (nF)</th>
<th>Film Thickness (Å)</th>
<th>Dielectric Constant εr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li/Ta</td>
<td>XTa</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0/1</td>
<td>1/1</td>
<td>Ta2O5</td>
<td>72</td>
<td>550</td>
<td>17.9</td>
</tr>
<tr>
<td>1/3</td>
<td>3/4</td>
<td>LiTaO3 + Ta2O5</td>
<td>59</td>
<td>750</td>
<td>20.0</td>
</tr>
<tr>
<td>1/1</td>
<td>1/2</td>
<td>LiTaO3</td>
<td>31</td>
<td>600</td>
<td>8.4</td>
</tr>
<tr>
<td>3/1</td>
<td>1/4</td>
<td>(Li3TaO4)</td>
<td>29</td>
<td>732.5</td>
<td>9.6</td>
</tr>
<tr>
<td>3/1</td>
<td>1/4</td>
<td>(Li3TaO4)</td>
<td>28</td>
<td>650</td>
<td>8.2</td>
</tr>
<tr>
<td>7/1</td>
<td>1/8</td>
<td>(Li7TaO6)</td>
<td>49</td>
<td>900</td>
<td>19.9</td>
</tr>
<tr>
<td>7/1</td>
<td>1/8</td>
<td>(Li7TaO6)</td>
<td>40</td>
<td>1250</td>
<td>22.6</td>
</tr>
<tr>
<td>7/1</td>
<td>1/8</td>
<td>(Li7TaO6)</td>
<td>48</td>
<td>1100</td>
<td>23.9</td>
</tr>
</tbody>
</table>

Unverifiable compounds listed in parentheses.

are consistent. The calculated value of the dielectric constant of Ta2O5 of 17.9 is in close agreement to the value of 25 found by Ling et al. (30). Introducing one mole of lithium for every three moles of tantalum (nominally, LiTa3O8) makes no significant improvement, although XRD seems to indicate that the film is composed of lithium tantalate and tantalum oxide. Increasing the mole ratio to one (LiTaO3) should produce a dielectric constant near 42, however, the calculated dielectric constant is a disappointingly low 8.4. The low dielectric constant is maintained until a mole ratio of seven is attained, where the constant rises again. However, XRD analysis of the lithium rich compositions was almost inconclusive, limiting the conclusions that can be drawn from the stoichiometry ranges.
Table 8. Lithium niobate films produced by sol-gels

<table>
<thead>
<tr>
<th>Mole Ratio Li/Nb</th>
<th>Mole Fraction X&lt;sub&gt;Nb&lt;/sub&gt;</th>
<th>Compound&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Film Capacitance (nF)</th>
<th>Film Thickness (Å)</th>
<th>Dielectric Constant ε&lt;sub&gt;r&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>0/1</td>
<td>1/1</td>
<td>Nb₂O₅</td>
<td>85.0</td>
<td>550</td>
<td>21.1</td>
</tr>
<tr>
<td>2/32</td>
<td>32/34</td>
<td>Nb₂O₅</td>
<td>10.9</td>
<td>1800</td>
<td>8.9</td>
</tr>
<tr>
<td>1/1</td>
<td>1/2</td>
<td>LiNbO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>48.0</td>
<td>700</td>
<td>15.2</td>
</tr>
<tr>
<td>1/1</td>
<td>1/2</td>
<td>LiNbO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>45.0</td>
<td>900</td>
<td>18.3</td>
</tr>
<tr>
<td>3/1</td>
<td>1/4</td>
<td>(Li₃ NbO&lt;sub&gt;4&lt;/sub&gt;)</td>
<td>32.0</td>
<td>1350</td>
<td>19.5</td>
</tr>
<tr>
<td>3/1</td>
<td>1/4</td>
<td>(Li₃ NbO&lt;sub&gt;4&lt;/sub&gt;)</td>
<td>21.0</td>
<td>1400</td>
<td>13.3</td>
</tr>
<tr>
<td>7/1</td>
<td>1/8</td>
<td>Li₃ NbO&lt;sub&gt;4&lt;/sub&gt; + LiNbO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>21.0</td>
<td>1600</td>
<td>15.2</td>
</tr>
<tr>
<td>7/1</td>
<td>1/8</td>
<td>Li₃ NbO&lt;sub&gt;4&lt;/sub&gt; + LiNbO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>30.0</td>
<td>1300</td>
<td>17.6</td>
</tr>
</tbody>
</table>

<sup>a</sup>Unverifiable compounds listed in parentheses.

**Lithium niobate**

Again, due to limited sol stability, films of LiNbO₃, Li₃ NbO₄, and Li₇ NbO₆ were duplicated. As shown in Table 8, the duplicated films gave consistent measurements. The calculated dielectric constants of LiNbO₃ of 15.2 and 18.3 are about half reported the value of 36. Except for the very low dielectric constant found at a lithium to niobium ratio of 2/32, no trend was apparent. The compound Li₂ Nb₃ O₈₁ is a high temperature phase, and XRD analysis of the film indicates that at ambient temperatures, the film is delta Nb₂O₅. Thus, the presence of free lithium in the niobia lattice, that not associated with the ceramic compound, appears to reduce the dielectric constant.
Auger electron spectroscopy

Auger electron spectroscopy (AES) was used to analyze the vertical composition of four of the barium titanate (BaTiO$_3$) films as a hole was sputtered through the film to the silicon wafer. A schematic diagram of the AES results is given in Figure 19. The film was about 500 Å thick. At the surface of the film, the approximate compositions are correct: Ba/Ti equals 1 and O/Ti equals 3. This composition remains constant through the top 80% of the film. However, the titanium is absent from the remaining 20% of the film profile. Silicon dioxide appears for only the 50 angstroms on the substrate surface, so it would seem that a reaction with silicon is not causing the inhomogeneity.

Since the titanium oxide comprises a gel network and the barium is dissolved in the liquid phase, which is interspersed throughout the titanium oxide gel network, the rheology of the system during spinning may be the cause of the differential layering. Gels, being thixotropic, change viscosity as the fluid flows over the surface of the substrate. The barium oxide, being free in the liquid, may be differentially separated from the titania polymers, by the changing viscosity of the gel. Indeed, SEM photographs of the films produced by successive layering of the sol show stratification caused by barium oxide layering at the bottom of each layer. Thus, the spinning of the film would seem to be responsible for the heterogeneity. This effect could most likely be minimized by a careful study of the interaction between sol viscosity and spinning conditions, and their individual effects upon differential separation of the bulk fluid of the sol at the surface of the substrate.
Energy dispersive spectroscopy

The elemental composition of all of the BaTiO$_3$ films was determined semi-quantitatively by energy dispersive spectroscopy (EDS) through the internal standards available in the analytical software. The elemental composition of the sintered films was found to be the same as that in the original sol, and the composition was constant across each film and from film to film. Thus, at least for the BaTiO$_3$ films, the elemental composition did not vary appreciably at different horizontal positions on the film.
Table 9. EDS results for one layer of barium titanate

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Si</td>
</tr>
<tr>
<td>500</td>
<td>75.5</td>
</tr>
<tr>
<td>600</td>
<td>81.7</td>
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<td>77.3</td>
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<tr>
<td>900</td>
<td>71.5</td>
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<tr>
<td>1000</td>
<td>69.1</td>
</tr>
</tbody>
</table>

The ethoxides of niobium and tantalum were of electronic grade, but, as shown in Table 9, EDS analysis of barium titanate films indicates that a significant concentration of chlorine can be present in the barium titanate films, even after calcination at 700°C. Residual chlorine is present in the reaction feedstock as a result of the reaction of titanium tetrachloride with ethanol to produce titanium ethoxide, and a significant amount of chlorine remains in the film after sintering at 500°C. However, the chlorine concentration decreases rapidly as the sintering temperature increases, becoming relatively constant at sintering temperatures above 700°C.
DISCUSSION

The sol-gel method to the production of ceramic oxide thin films appears to be effective as a means of applying films of the materials studied. The sol-gels themselves are reproducible. Duplication of various sol-gels leads to identical properties, i.e., viscosity and gelation time. The films, themselves, are also reproducible, as has been shown with the duplicated films of the lithium niobates and lithium tantalates which had the same thickness, capacitance, and dielectric constants. Each step in the procedure — the liquid phase condensation of the sol-gel, the spinning and drying of the film, successive layering, and sintering — had to be analyzed for its effect on the sintered film to determine the effectiveness of applying films by the sol-gel process.

While the reaction of the metal alkoxides are similar, different metal oxides show dissimilar results under uniform conditions. For example, although the tantalum gel number 19 from Table 3 and the niobium gel number 2 from Table 5 have identical reaction conditions, the tantalum gels in a week, while the niobium requires a longer time to gel. The same comparison is exhibited by the similar reaction conditions of the tantalum gel number 17 from Table 3, which gels in 4 days, and the titanium gel number 4 from Table 4, which gels in 2 months. While, in general, the condensation of the metal alkoxides is similar for all metal alkoxides involved, each metal alkoxide has its
own hydrolysis and condensation rate. Little work has been done on the kinetics of these reactions. Yet, for preparing sol-gels of mixed cations, the kinetics of the hydrolysis and condensation reactions is extremely important in being able to make stable sols. A great deal more work is needed on the kinetics of these reactions.

The ability to prepare coherent films of $\text{BaTi}_4\text{O}_{11}$ and $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ was one of the more important results of this work. Both are important as microwave dielectric resonator filters. Both have been reported as having been prepared in bulk, but no films have been reported. Ritter et al. (56) have recently reported that $\text{BaTi}_4\text{O}_{11}$ is a low-temperature phase and that its decomposition temperature at 100 kPa (1 atm) is 850–900°C. Thus the ability to prepare a coherent film of this material at 700°C by the sol-gel method is very important. This low sintering temperature is a characteristic of the sol-gel process and is possible because of the very small particle size of the precursor material.

In summary, it has been shown possible to prepare thin films of various members of the family of barium titanates, lithium niobates, and lithium tantalates. The films adhered well to the substrate, were coherent, and had excellent physical properties. The electrical property measurements were disappointing, but working with very high purity starting materials under carefully controlled conditions would most likely produce films with substantially better electrical characterization.

The model for the application of sol-gel derived ceramic oxide films on a spinning silicon substrate,
\[ d = (w)^{-0.5}(2000 \log(\mu) + 350), \]

is purely empirical, but does adequately describe the data obtained. The largest deviations of the data from the line are about 300 angstroms. While this translates to an error of 10 to 15% at viscosities around 25 cp, it is on the order of 60 to 70% for viscosities around 0.8 cp. However, it is important to remember that while the alpha step profilometer reproduces the film profile with high accuracy, the sample preparation and the measurement technique can produce surface variations of up to 200 or 300 angstroms. Thus, while the model does not account for all the variation, no doubt a result of the particular oxide, solvent, and sol concentration, it is adequate within the constraints of the sample preparation and measurement techniques available that were used to obtain the data from which the correlation was derived.

Furthermore, as the viscosity reaches about 15 cp with application speeds of 3000 rpm, crazing of the films begins to become evident as the spinning speed is insufficient to develop sufficient radial flow before solvent evaporation leads to drying of the film. Reducing the spinning speed has the same effect, as was seen with the sol of the highest viscosity (26.2 cp), which developed crazed films at spinning speeds of 6000, 4000, and 3000 rpm, but could not even develop a film at a spinning speed of 1000 rpm. Thus, while at constant spinning speeds, the lower limit of the film thickness would occur at a sol viscosity equal to the solvent viscosity (an infinite dilution), an upper limit would be established by the inter-dependent fluid flow and evaporation
mechanisms present in the spinning film.

Although the preparation of the single component sols as single component films was an easy process, producing a binary cation oxide ceramic film was not as straightforward. The correct stoichiometric ratio in the sol does not necessarily produce the desired binary compound. For instance, both lithium niobate and lithium tantalate sols can be produced by either mixing the lithium solution with the hydrolyzed sol or hydrolyzing the mixed metal alkoxide solution; but, only hydrolyzing the mixed cation solution produces the desired compound. The addition of the lithium solution to the sol leads to a bi-phasic film; as the lithium probably does not mix intimately into the already hydrolyzed tantalum sol network, as is indicated by the limited shelf life of the sols. Mixing the alkoxides prior to hydrolysis allows for some degree of complexing to take place before the cations are hydrolyzed, allowing the lithium to be a part of the metal oxide network, as evidenced by the increased stability of the sols. However, the barium titanates precursor sols produced compounds with the stoichiometry of the precursor sol, even if the sol had limited stability.

One of the objectives of this work was to observe the trends of the dielectric constants of known compounds of the barium titanates, lithium niobates, and lithium tantalates as the stoichiometry was varied. However, no trends were apparent in any of the families tested. One of the problems is that the multiple application of the sols to produce thicker films did not always produce films thick enough to determine the
crystal structure with XRD, leaving in question the exact crystalline nature of the sol-gel derived film. Other methods of analysis, particularly small angle x-ray scattering would have made it easier to analyze these films.

The calculated dielectric constants of the lithium tantalates and lithium niobates were within the range of the constants reported in the literature, but no trends were readily apparent. However, as dielectric materials, the constants are too low to be of great industrial importance. Evaluation of the optical properties might be a more appropriate index as to the applicability of the sol-gel method of producing both the lithium niobates and the lithium tantalates. It is possible that the films with high lithium contents actually exist as mixed lithium oxide and lithium tantalate or lithium niobate ceramics. If the lithium oxide did not disrupt the lattice of the other constituent oxide, the dielectric constant may be impervious to the addition. Unfortunately, the lithium niobates and lithium tantalates with high lithium contents did not form films thick enough for definitive XRD analysis to be obtained. Also, the sols had only limited stability. Thus, although they were stable long enough to spin films, it was not possible to dry the bulk sol and calcine it to obtain an XRD analysis of the bulk powder.

While they were low, the calculated dielectric constants of the barium titanates were within typical ranges reported. Recall that at a lithium to niobium ratio of 2/32, XRD indicates that the film was not $\text{Li}_2\text{Nb}_{32}\text{O}_{81}$, but $\text{Nb}_2\text{O}_5$. Thus, it would be expected that the film would
have a calculated dielectric constant near that calculated for \( \text{Nb}_2\text{O}_5 \). However, the presence of lithium in the niobia lattice had a detrimental effect on the dielectric constant of niobia.

It is possible that concentrations of chlorine in the barium titanate films could have a detrimental effect on the dielectric constant in the same manner that lithium had on the dielectric constant of niobia. Since the barium titanate sols were stable indefinitely, it was possible to dry and calcine the gel to analyze the bulk composition of the powder by XRD. Powders done this way yielded the same crystal structure as the corresponding films, indicating that XRD analysis of the sol-gel derived powder is an acceptable method of determining the composition of the ceramic film. XRD analysis of the barium titanates also showed that calcining the stable sols does lead to the barium titanate of the same stoichiometry as existed in the precursor sol.
CONCLUSIONS

The sol-gel route to the production of ceramic oxide films is both versatile and reproducible. This is readily apparent in the variety of compounds amenable to the sol-gel process. These include binary cation oxides as well as the single cation oxides.

The films of niobia, tantala, titania, yttria, and zirconia are readily produced on silicon wafers. Using these as a basis, mixed cation compounds such as barium titanate, bismuth germanium oxide, lithium niobate, and lithium tantalate were made. Films of barium titanate, lithium niobate, and lithium tantalate could be made in a wide variety of stoichiometries. However, an analytical method more sensitive than x-ray diffraction needs to be available for crystallographic determination before in depth characterization of these films can be done.

Application of films on spinning substrates worked very well. The films were coherent, smooth, and uniform. As with gel monoliths, production of thicker films, by using more viscous sols and lower spinning speeds during film application, led to stresses in the film due to evaporation rate differences within the film, resulting in crazing. However, maintaining high spinning speeds and less viscous sols facilitates the production of thinner films, where the drying does not appear to be a problem.

While the empirical model,
\[ d = (w)^{-0.5}(2000 \log(\mu) + 350), \]
does adequately describe the data within the reliability of the film thickness measuring technique, it does not account for deviations from the model as a result of the specific metal oxide, solvent, or concentration. The interrelationship of the gelation of the sol and the solvent evaporation from the sol with the rheology during film application needs to be understood to fully exploit production of sol-gel derived films. Rather than relying on the trial-and-error method of achieving the desired film thickness, a model that allows for the contributions of all the sol variables would lead to the understanding of the film application process and allow for the development of more exacting electronic devices.

While the dielectric constants of the lithium niobate and lithium tantalate films were well within the reported values, the constants of the barium titanates were disappointingly low. Since the presence of ionic impurities within the oxide lattice would be expected to alter the electrical properties, the presence of chlorine in the barium titanate films is the most probable culprit for the disappointing performance of the barium titanate films. The use of purified raw materials, as was used in deriving the lithium niobate and lithium tantalate, would be the logical recourse. This could be accomplished by the vacuum distillation of the titanium ethoxide and the recrystallization of the barium isopropoxide.

The sol-gel process can easily be expanded to produce films of any material which can be obtained as a sol-gel. This includes the new
super-conductive family of the lanthanum-barium-copper oxides and yttrium-barium-copper oxides. However, the desired cations must be available as either a liquid or in solution before the acid catalyzed hydrolysis can be accomplished. Once a sol was produced, sol-gel processing could be used to produce thin films or fibers, as well as monoliths or powders.


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