USES OF CERAMICS IN MICROELECTRONICS

A SURVEY

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
USES OF CERAMICS IN MICROELECTRONICS

A SURVEY

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Prepared under contract for the NASA Technology Utilization Office
Foreword

This survey is one of a series issued by the National Aeronautics and Space Administration as part of its Technology Utilization Program to disseminate information useful for general industrial applications. *Uses of Ceramics in Microelectronics* is addressed to management personnel concerned with electronic circuitry. It describes advances in the state of the art of passive components (insulators, resistors, and capacitors) of electronic devices. Requirements for the exploration of space have accelerated such advances, and they can be helpful in many additional ways.

The electronics industry has become highly dependent on the interface between materials and devices. Improvements in passive components have kept pace with advances in active devices. Unanticipated benefits in design flexibility and tolerances to adverse environments have been discovered. Mass production of passive components can bring about wider use of ceramics in microelectronic systems. Both industrial processes and consumer products can thereby be improved.

In the final chapter the authors have examined the interface between materials and devices as it affects microcircuitry, and have shown how technology is transferable from the aerospace community to many broad tasks in fulfilling human needs.

*Director*

*Technology Utilization Office*
Acknowledgments

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CHAPTER 1

Introduction

PURPOSE AND SCOPE

Microelectronics technology is the frontier of the multi-billion-dollar electronic components industry. Its development has been expedited in part by space requirements for small volume and low weight with high reliability. From the earliest innovations in microelectronics in the 1950's through every stage of the advances, ceramics have been a significant factor. As semiconductors advanced from discrete devices to the several varieties of integrated circuitry, ceramic technology continued to be helpful in problem solving. Its contributions included not only materials but also special processing and techniques for printing, metallizing, joining, and sealing. Materials ranged from alumina ceramics for substrates to lead oxide glasses for varied functions.

An example of a ceramic-forming process which was ready to meet the escalating demands of microelectronics for large quantities, design complexity, and surface finish is the "tape" method applied to making substrates. Thick-film printing formulas and techniques were available from the decoration of glass and china, and had been continually improved. The molymanganese metallizing procedures were taken over from the sealing practices developed for ceramic vacuum-tube technology. So intimate has been the interdependence of ceramics and circuitry that one descriptive adjective applied to thick-film hybrid circuits is "ceramic-based."

The purpose of this survey is to examine the properties and behavior of ceramic materials as used in components for electronic circuitry. By citations of specific projects and reports, NASA contributions to materials, components, and processing for microelectronics are identified. The effects of these advances on present and future directions for microelectronics and its applications in industry and consumer goods will be appraised, suggesting how they may further promote product developments and how the processing innovations may be useful in other technologies.

Although ceramics have played a critical part in every era and
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advance in electronics, this review will be limited mainly to the current uses of ceramics for passive components in microelectronics. The reason is twofold—to keep the text to a reasonable size and to be involved mainly with a frontier of electronics rather than historical aspects.

Some dynamic forefronts which are also dependent on the special properties of ceramics will also be bypassed. These include such topics as lasers, electro-optics including nonlinear optoelectronics, fiber optic faceplates for cathode-ray tubes, other ceramic elements in cathode-ray tubes, ceramic receiving and power tubes, high-temperature circuitry such as thermionic integrated micro-modules (TIMMS), radiation-tolerant electronics, transducers, amorphous semiconductors, magnetics, and many other material or device innovations.

DEFINITION OF CERAMICS

To make clear what is meant by the term "ceramics," the most straightforward definition embodying the current scope of the field is (ref. 1) : "A ceramic is an inorganic nonmetallic material or article. Ceramics may be polycrystals, glasses, or combinations thereof, or single crystals."

By this definition, glasses are a subgroup of ceramics. To talk of ceramics and glasses is redundant, as is the term "glass-ceramics." Yet in the electrical industries a distinction has been made between ceramics and glasses. In practice, the glasses and crystalline ceramics are competitive and differ enough in structure, properties, and behavior to justify a distinction between them.

The broad interpretation includes all solid materials which are not metallic or organic as ceramics. With the current emphasis on materials science and engineering, such distinctions tend to become blurred, and the emphasis is on the impartial selection of the best material, or composite of materials, for the application. Microelectronics particularly may be looked upon as the offspring of the materials science concept. It requires materials of every class, combined to satisfy exacting demands for electrical, magnetic, mechanical, chemical, optical, acoustical, radiation, and energy transformation performance.

As a consequence, many technologies and all classes of materials have contributed to microelectronics, and no desire exists to overemphasize the contributions of ceramics. Truthfully it may
be said that without ceramics there would be no electronics, and that all attempts to design ceramics out of circuitry circle back to a dependence on ceramic materials in some new form.

CERAMICS IN ELECTRONIC SYSTEMS

Ceramics in the glassy state have been essential materials for electronics from the time of the first vacuum tubes (ref. 2). With the requirements for higher temperatures and frequencies, crystalline ceramics came into use as envelopes and spacers in both power and receiving tubes (refs. 3 and 4). With the advent of solid-state components and circuitry, the materials and technologies developed for tubes were applied as substrates, enclosures, and encapsulants. New applications for ceramics in electronics and microelectronics have also appeared in the forms of resistors, capacitors, semiconductors, photoconductors, dielectric and protective coatings, and many other usages.

Table I presents a classification of ceramics for electronics as drafted in December 1961 (ref. 5). Since then, the surge of research has carried ceramic materials into new areas of chemical compositions, physical structures, properties, and applications. Rapid developments in microelectronics (whether thin-film, thick-film, integrated circuitry or hybrids) required ceramic materials and processing for circuit elements, substrates, and protection against hostile environments.

The rapid changes in design requirements and the many competing approaches to circuits of high component density have left the materials and components producers and the circuit and device assembly specialists bewildered about which directions to follow in research, development, and manufacturing (ref. 6).

An example of the multiple choices among competing materials can be seen in ceramics for substrates. Pioneering researchers in thin films almost invariably selected ordinary glass microscope slides as the substrate because of their availability and convenient size. With accumulated experience, it was realized that sodium ions from the soda-lime-silica glass could diffuse into the active components under the influence of temperature and electric fields. These mobile ions damaged the reliability of the circuits. Other shortcomings of soda-lime glass included low strength, restricted maximum operating temperature, and low thermal conductivity. Replacement of soda-lime glass by borosilicate or aluminosilicate glasses low in alkalies, or by fused silica or Vycor glasses helped with the chemical disturbances, but introduced undesirable phys-

### Table I. Classification of Ceramics for Electronics

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<td>Linear</td>
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<td>Permeability</td>
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<td>Resistivity</td>
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<td>Dissipation factor</td>
<td>Dielectric losses</td>
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<td>High permittivity</td>
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**Properties:**
- Resistivity
- Magnetic permeability
- Dielectric losses
- Dissipation factor
- Dielectric constant
- Mechanical strength
- Thermal expansion
- Thermal conductivity
- Permittivity
- Thermal diffusivity
- Electrical conductivity
- Magnetic susceptibility
- Switching coefficients
### Temperature Coefficients
- Frequency dependence
- Density and porosity
- Physical permeability

<table>
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<th>Temperature coefficients</th>
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<td>Magnet cores</td>
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<td>Transducers</td>
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<td>Memory devices</td>
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<td>Electrothermoclines</td>
<td>Bushings (lead throughs)</td>
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<td>Delay lines</td>
<td>Thermoelectric devices</td>
<td>Electrode coatings</td>
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<td>Microwave non-reciprocal devices and filters</td>
<td>Hall effect devices</td>
<td>Printed circuits</td>
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<td>Antennas</td>
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<td>Rectifiers</td>
<td>Dielectric films</td>
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<td>Attenuators</td>
<td>Linear circuit elements</td>
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<td>Resisters:</td>
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<td>Thermistors</td>
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<td>Magnetoresistors</td>
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<td>Lumistors</td>
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<td>Cathodes (electron emitters)</td>
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### Illustrative Materials
- Steatites, high aluminas, glasses, bonded micas, crystallized glasses, rutile, titanates (Mg, Zn)
- Titanates (Bo, Sr), niobates, lead zirconate titanates, zirconates
- Ferrites, garnets, magneto-plumbites
- Oxides, sulfides, tellurides, carbides, intermetallics, borides, silicides
- Glass-metal, cermets, ceramic-metallizing films, metal, metal electrodes, tin oxide films

*From American Society for Testing and Materials Subcommittee Proposal.*
ical stresses derived from the mismatch in thermal expansion between the substrate and the attached circuit elements.

Alumina ceramics next came to the fore as a substrate material. The manufacturing facilities were available because of the earlier demands for alumina in electron tubes. Strengths were an order of magnitude higher than for glasses. Electrical insulating properties were superior. Thermal expansion was in a useful range. When the surfaces of the early products were judged not sufficiently smooth for thin-film requirements, the problem was solved by glazing with compositions which did not appear to be objectionable in contributing mobile ions or debasing electrical properties. Recently, considerable advances have been made in achieving acceptable surface finishes on unglazed alumina ceramics. Users have been educated to the wide ranges of chemical compositions, microstructures, and surface textures available from different suppliers, or from a single supplier under different trade designations. Sapphire, a single-crystal form of alumina, is also being appraised as a substrate material.

With higher component densities and power levels, the transport of heat away from the circuit became a problem. Beryllia substrates were adopted because of their outstandingly high thermal conductivities. However, their use has been limited by their high costs. In some applications, even beryllia's thermal conductivity has been inadequate, and copper metal coated with a thin electrically insulating layer of ceramic has been utilized as a substrate.

Meanwhile, for mass-consumed devices with less stringent requirements, consideration is being given to lower cost alternatives to alumina ceramics, such as steatites, porcelains, or barium titanate. Steatite, glass-bonded mica, and barium titanate ceramics already have a history of use for printed circuit boards, as have various polymers and glass-fiber-reinforced plastics. Recrystallized glasses are also being appraised as free-standing substrates and as coatings. In addition to cost savings, closer scrutiny may expose some technical advantages for such alternatives to alumina.

With so many choices in materials, even for inert elements such as substrates, it is no wonder that component and circuit designers are calling for guidance from specialists in ceramics for electronics. A major part of the dilemma has been that the formerly sharp divisions between materials, components, devices, and systems are being wiped out by the advances in microelectronics (fig. 1) (ref. 6). Individual specialists can no longer be
INTRODUCTION

FIGURE 1.—Rates of development of electronic systems. These curves suggest how knowledge intensifies and broadens as electronics progresses to microcircuits. Two things speed up the innovation process (17 yr for transistors versus 40 yr for tubes): First, knowledge intensifies and broadens among specialists in materials, devices, circuits, and systems; second, these specialists begin to share common knowledge as symbolized by the overlapping of the specialist areas on the curves.

trained or maintained in isolated disciplines. They must learn to surmount the old knowledge barriers and to operate in multi-disciplinary environments.

Correspondingly, the old divisions of industries into specialties are being wiped out. Materials suppliers must decide whether to acquire competence in making components. Components producers are faced with decisions about whether to process their own material, on one hand, or to assemble and market circuits and devices or even systems, on the other.

The situation was similar from about 1946 to 1955 when ceramic-metal electron tubes were under development and in early usage. The electronic companies had to decide whether to make or buy ceramics, whether to take the responsibility for innovation in materials and processes or to be dependent on materials companies. The ceramic companies were also uncertain about the safe rate at which to invest in scaling up their manufacturing facilities and in research and development on improved materials and processes. Questions hung over the decisionmaking about what compositions of ceramics to adopt and what sealing process was best.
This was a case of giant electronic companies making demands for high technical performance on small materials and subassembly suppliers. In self-defense, many of the largest electronics manufacturers did invest in engineering model shops and small-scale manufacturing plants to assure their supplies of ceramics and seal structures.

Looking back, it can be seen that most of the electron-tube manufacturers returned to buying their ceramics from the surviving ceramic suppliers. Similar histories can be recounted about the supply of ferrites for television or computers, or of barium titanate ceramics for capacitors. What will happen in the microelectronics dilemma is not clear from history. However, it can be predicted that materials will continue to play a critical role wherever the responsibilities are vested for their selection, optimization, innovation, application, and manufacture.

The rapid advances in microelectronics have been greatly influenced by aerospace requirements. Savings in weight and in volume have been critical, but at the same time tolerance to high temperatures, radiations, and mechanical and thermal shocks has been demanded. The impetus for more reliable, more compact electronics has come not only from NASA but also from military and industrial markets. In turn, new applications for microcircuitry are busting out all over, in the auto, appliance, computer, telephone, and other industries.

The need is apparent for a review of the current role of ceramics in microelectronics to help decisionmakers in industry and in Government agencies appraise the trends in material requirements and their interactions with trends in components and circuitry. In the following pages such a survey is presented in terms of the functions of insulators, resistors, and capacitors, and their combination into microcircuits.
Ceramic and Glass Insulators

Of all of the insulating materials used in electronics, glass is probably most familiar. People are aware of its transparency, insulating properties, and durability. Thanks to its luster, its smoothness, and its formability, who has not admired glass crystal artware? Dropping a glass object also establishes its brittle nature. Lamps are an obvious application of the electrical insulating qualities of glass. The ranges of properties available in glasses are extended and broadened in multicrystalline ceramics and enable these classes of material to satisfy many critical property requirements as electrical insulators.

The purpose of insulators in electrical circuits may be to provide mechanical support, electrical insulation, environmental protection, and/or heat dissipation. Depending upon the application, one or some combination of the above functions dictates the technical requirements. To meet these needs, a variety of insulating materials has been developed. Many of these are available in varying grades, so that the lowest cost material may be used for each application.

**TYPES OF ELECTRICAL INSULATION**

Insulating materials for electrical applications occur in four broad classifications: ceramics, plastics, liquids, and gases. Ceramic insulators serve where high voltages, humid conditions, high temperatures, stability, or cost factors dictate their use. They are employed extensively in microelectronic circuitry not only because of their excellent physical properties but also on account of their adaptability to microelectronic processing. Plastic insulation materials embrace paper- or fabric-based phenolic laminates, melamines, polyesters, epoxies, silicones, diallyl phthalate, as well as other organic compounds. Their advantages lie in ease and versatility of forming, availability in flexible sheets, adaptability to a wide range of designs, and ability to withstand mechanical abuse. Because of their permeability to moisture, the
plastic materials must frequently be treated with waxes or varnishes. The more modern plastics such as the silicones, polyesters, polytetrafluoroethylene (PTFE), and vinyls usually do not require such treatments, but still are less effective than ceramics for protection against moisture penetration. Liquids are used in such applications as oil-filled transformers for high-voltage and high-power uses. Gases are used in electron tubes, cables, transformers, and special relays. The advantages of the selected liquids and gases are high dielectric strength, that they are self-healing after arcing, and high thermal conductivity.

A comparison of the properties of a number of representative insulating solids is shown in table II (ref. 7). In general, the organic-containing materials (groups I, II, and III) have good dielectric strength, low dielectric constant, and low operating temperatures. With the exception of PTFE, they all show some moisture absorption, and except for the high-strength polyester films, they must be incorporated in glass-fiber composites for adequate tensile strengths. The dissipation factor varies from 0.0002 for polyethylene to 0.045 for phenolic-paper laminates. The ceramic and glass-based insulation materials represented in group IV have high dielectric strengths, low dissipation factors, high operating temperatures, and essentially zero moisture absorption. Exceptions to these generalizations are the small moisture absorption of the glass-bonded mica and the low dielectric strength of the titanium dioxide. Dielectric constants range from 3.85 for fused silica to 96 for titania.

**CERAMIC INSULATORS**

Ceramic insulators will be examined here in terms of advantages, disadvantages, and principal applications. A summation of representative properties for the various types is shown in tables III to VI (ref. 8).

The alumina ceramics range from aluminosilicate glass-bonded porcelains starting at about 50 wt % alumina to glass-free, multicrystalline 99.9% alumina bodies, and to the purest sapphire si-

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It cannot be stressed too strongly that any property data cited for ceramics are representative only and should not be utilized in engineering design. At the present state of the art, variations in values for composition and structure-sensitive properties, such as loss factor and flexural strength, can be very large for a given class of compositions, from manufacturer to manufacturer, and from batch to batch. However, improved understanding of microstructure and control is improving reproducibility. Property data cited for metals, such as in figures 2 and 3, are also representative only and can vary between suppliers and between lots.
### Table II—Properties of Representative Insulating Solids

<table>
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<tr>
<th>Material</th>
<th>Dielectric strength at low frequencies (sample 0.000 in. thick), V/mil</th>
<th>Dissipation factor, tanδ at 10⁸ cps</th>
<th>Dielectric constant at 10⁸ cps</th>
<th>Maximum operating temperature, °C</th>
<th>Tensile strength, lb/in²</th>
<th>Moisture absorption, percent</th>
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<td><strong>Group I—plastics:</strong></td>
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<tr>
<td>Polyethylene</td>
<td>300</td>
<td>0.0002</td>
<td>2.25</td>
<td>75</td>
<td>1 800</td>
<td>0.03</td>
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<tr>
<td>Polytetrafluoroethylene (PTFE)</td>
<td>400</td>
<td>0.0003</td>
<td>2.0</td>
<td>200</td>
<td>2 000</td>
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*a Measured on maximum available thickness = 0.0075 in.*
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<td>7.8 × 10^-4</td>
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<td>25°-700° C</td>
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<td>8.2 × 10^-4</td>
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<td>25°-900° C</td>
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<td>8.4 × 10^-4</td>
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<td>8.5 × 10^-4</td>
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* Compiled from various sources; values will vary depending on source.
### Table IV. Representative Electrical Properties of Alumina Ceramics, Sapphire, and Beryllia Ceramics

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<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>Alumina</th>
<th>Sapphire</th>
<th>Beryllia</th>
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<td>96% Al₂O₃</td>
<td>99.5% Al₂O₃</td>
<td>99.5% BeO</td>
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<td>Dielectric strength, 60-cycle ac. test disks ½ in. thick</td>
<td>v/mil kv/mm</td>
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<td>&gt;10¹⁴</td>
<td>&gt;10¹⁴</td>
<td>&gt;10¹⁴</td>
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<tr>
<td>25°C C</td>
<td></td>
<td>100°C C</td>
<td>300°C C</td>
<td>500°C C</td>
</tr>
<tr>
<td>60 cycles</td>
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<td>25°C C</td>
</tr>
<tr>
<td>1 Me C</td>
<td>9.3</td>
<td>9.5</td>
<td>10.8</td>
<td>22.4</td>
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<tr>
<td>100 Me C</td>
<td>9.3</td>
<td>9.4</td>
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<td>1000  Me</td>
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* Applied for various sources; values vary according to source.
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<th>Forsterite 2MgO·SiO₂</th>
<th>Cordierite 2MgO·2Al₂O₃·5SiO₂</th>
<th>Zircon ZrO₂·SiO₂</th>
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<td>7.8 × 10⁻⁴</td>
<td>11.2 × 10⁻⁴</td>
<td>3.3 × 10⁻⁴</td>
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<td>Magnesia 99.5%</td>
<td>Fused silica SiO₂</td>
</tr>
<tr>
<td>--------------------------------</td>
<td>------</td>
<td>------</td>
<td>---------------------</td>
<td>----------------</td>
<td>------------------</td>
</tr>
<tr>
<td><strong>Mechanical properties:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Specific gravity</td>
<td></td>
<td>4.0</td>
<td>2.4</td>
<td>3.6</td>
<td>2.65</td>
</tr>
<tr>
<td>Hardness</td>
<td>Mohs' scale</td>
<td>8</td>
<td>6</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>psi</td>
<td>kg/cm²</td>
<td>7500 530</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Compressive strength</td>
<td>psi</td>
<td>kg/cm²</td>
<td>100 000 7030</td>
<td>8000 560</td>
<td>20 000 14 100</td>
</tr>
<tr>
<td>Flexural strength</td>
<td>psi</td>
<td>kg/cm²</td>
<td>20 000 1400</td>
<td>2000 140</td>
<td>25 000 1760</td>
</tr>
<tr>
<td>Resistance to impact</td>
<td>in.-lb</td>
<td>m-kg</td>
<td>6.5 .075</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Modulus of elasticity</td>
<td>psi × 10⁶</td>
<td>kg/cm² × 10⁶</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shear modulus</td>
<td>psi × 10⁶</td>
<td>kg/cm² × 10⁶</td>
<td></td>
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<td></td>
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<tr>
<td>Poisson's ratio</td>
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<tr>
<td><strong>Thermal properties:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Safe temperature at continuous heat</td>
<td>°C</td>
<td>1000</td>
<td>1600</td>
<td>1600</td>
<td>900</td>
</tr>
<tr>
<td></td>
<td>°F</td>
<td>1832</td>
<td>2912</td>
<td>2912</td>
<td>1650</td>
</tr>
<tr>
<td>Thermal expansion, linear coefficient</td>
<td>Per °C</td>
<td>25°-300° C</td>
<td>8.3 × 10⁻⁶</td>
<td>11.2 × 10⁻⁶</td>
<td>11.4 × 10⁻⁶</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25°-700° C</td>
<td>9.0 × 10⁻⁶</td>
<td>12.6 × 10⁻⁶</td>
<td>12.5 × 10⁻⁶</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25°-900° C</td>
<td></td>
<td></td>
<td>0.50 × 10⁻⁶</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25° C</td>
<td>Btu in./hr</td>
<td>cal cm/sec</td>
<td></td>
<td>117</td>
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</tr>
<tr>
<td>300° C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.004</td>
</tr>
<tr>
<td>500° C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>800° C</td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>

* Compiled from various sources; values will vary depending on source.
## Table VI. Representative Electrical Properties of Miscellaneous Ceramics and Fused Silica

<table>
<thead>
<tr>
<th>Property</th>
<th>Fused silica SiO₂</th>
<th>High purity Titania TiO₂</th>
<th>2MgO-2Al₂O₃-SiO₂</th>
<th>2MgO-5Al₂O₃-SiO₂</th>
<th>2MgO-SiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume resistivity, mohm cm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100°C</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
</tr>
<tr>
<td>200°C</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
</tr>
<tr>
<td>300°C</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
</tr>
<tr>
<td>400°C</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
</tr>
<tr>
<td>500°C</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
</tr>
<tr>
<td>600°C</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
</tr>
<tr>
<td>Dielectric constant, µf/in.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100°C</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
</tr>
<tr>
<td>200°C</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
</tr>
<tr>
<td>300°C</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
</tr>
<tr>
<td>400°C</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
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<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
</tr>
<tr>
<td>500°C</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
</tr>
<tr>
<td>600°C</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
</tr>
<tr>
<td>Dielectric strength, mV/µC/µm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100°C</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
</tr>
<tr>
<td>200°C</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
</tr>
<tr>
<td>300°C</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
</tr>
<tr>
<td>400°C</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
</tr>
<tr>
<td>500°C</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
</tr>
<tr>
<td>600°C</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
<td>&gt;10⁸</td>
</tr>
</tbody>
</table>

**Note:** Values in the table are approximate and may vary depending on the specific material and conditions tested.
gle. crystals which are essentially all aluminum oxide, except for stray impurity atoms. The alumina ceramic family offers a combination of desirable properties that has led to widespread use and assures a promising future (refs. 9 and 10). These include

1. Electrical properties: high resistance, low losses, and high dielectric strength
2. Mechanical properties: high compressive, tensile, and flexural strength; high impact strength, and high hardness
3. Thermal properties: intermediate thermal expansion coefficient (TCE) that enables sealing to many metals and matching components, good thermal conductivity, good thermal shock resistance, and good high-temperature properties
4. Chemical properties: extremely stable and surface capable of withstanding harsh chemicals and cleaning procedures
5. Textural properties: impermeable to all gases, available in a range of grain sizes and surface finishes, and can be polished or glazed.

Alumina ceramics are very widely used for high-performance electronic applications because of their excellent properties and moderate cost. Typical thermal expansion characteristics of alumina are compared in figure 2 to other metals and ceramics used in electronics (ref. 11). The compatibility of alumina with Kovar® is one of its principal advantages. Disadvantages include high processing temperatures and expensive machining costs owing to extreme hardness.

Beryllia ceramics are outstanding because of their high thermal conductivity (fig. 3). For applications where high heat conductivity is a requisite, such as heat sinks for thermally sensitive components or high power dissipation in a limited space, beryllia ceramics are often essential (ref. 12). When used as an insulator, the low dielectric constant is also an asset in reducing crosstalk between conductors and in maintaining high signal propagation.

Beryllia ceramics are similar in many respects to the alumina ceramics but strength is lower, and care must be exercised in their use because of the toxicity of beryllia powders. The cost of beryllia ceramics tends to be higher than that of alumina ceramics on account of the safety facilities needed in their manufacture and the higher raw material costs.

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Figure 2.—Thermal expansion of various metals and ceramics.

Figure 3.—Thermal conductivity of various metals.
Steatite porcelains were developed as an improvement on traditional clay-feldspar-quartz electrical porcelains in order to decrease losses, especially at higher frequencies (megacycle range). They are relatively easy to machine, but their limitations lie in a relatively low thermal shock resistance due to high TCE and low strength compared to alumina ceramics. Steatite ceramics can, however, be made very economically and are widely used for many general-purpose insulators.

Forsterite ceramics were introduced as an improvement over steatite ceramics. They have higher resistivity, higher strength, lower losses at microwave frequencies and can be used at higher temperatures for more critical applications, such as high-temperature (HT) electron tubes and HT circuitry. Their higher thermal expansion coefficient matches those of many metals but causes thermal shock problems. Two families are utilized in forsterite ceramics, one matching the thermal expansion of certain chrome-iron alloys and the other matching titanium. The volume resistivities of various ceramics are shown in figure 4 where the superior high-temperature resistivity of the forsterite ceramics over steatite and even 96% alumina is evident (ref. 11); but, as noted previously, the data should be viewed cautiously.

Cordierite ceramics are outstanding for their thermal shock resistance. Porous cordierite ceramics are widely used for heating-wire supports, and are also available as dense ceramics. Since metals are higher in thermal expansion than cordierite, sealing to this ceramic is difficult.

Zircon, titania, and magnesia ceramics are not as widely used in electronics as the previously mentioned ceramics. However, applications are occasionally justified by some specific property. For example, the ability to be reduced to a semiconducting state leads to some uses of titania ceramics. Magnesia is used as the insulation in electrical heating elements, special thermocouples, and leads for high-temperature instrumentation. High electrical resistivity, relatively good thermal conductivity, and low hardness all contribute to its desirability for this purpose.

While virtually all commercial ceramics have some porosity due to gases entrapped during processing, pore-free grades of alumina (ref. 13) and yttrium oxide (ref. 14) are available. These are made from high-purity oxides, and they are chemically modified to enable sintering to full density. Densification and grain growth during processing are controlled so that all gas atoms in pores can diffuse along grain boundaries to the surface of the ceramic. Limited use has been made of these materials for elec-
USE OF CERAMICS IN MICROELECTRONICS

Figure 4.—Volume resistivity of various ceramics.

Electronic applications on account of their high cost and newness. Other oxides, including all of the rare earths, are being developed as full-density, multicrystalline ceramics.

Sapphire is used where its unique properties offer advantages. Since it contains no fluxes and is a single crystal, it has no porosity or grain boundaries. Its crystal structure permits its use as a substrate for epitaxial growth of single-crystal films of materials having similar lattice dimensions. Single-crystal spinel, beryllia, and quartz can also be used as substrates for epitaxial growth of
single-crystal films. Even diamond crystals are being utilized for substrates and heat sinks (ref. 15).

Other types of ceramics such as boron nitride, thoria, etc., are in limited use as insulators where unique properties fit them to specialized applications.

GLASS INSULATORS

Glasses in the form of sheet, tubing, powders, pastes, films, etc., are used in electronics for multiple purposes, most often for electrical insulation and sealing. In the insulation category, glasses provide the same functions as any other insulator; e.g., mechanical support, electrical insulation, environmental protection, and heat dissipation. Glasses have advantages in high resistivity, versatility in size and shape, fair mechanical strength, and low cost, but are not as rugged as most ceramics. Their electrical resistance at room temperature is high, but rapidly decreases with increased temperature or high humidity. Lossiness generally increases with higher frequencies. Environmental protection is excellent at lower temperatures, but diffusion of impurities through glasses can occur at relatively low temperatures (~500° C). As a result of their amorphous structures, glasses are low in thermal conductivity, about one-sixteenth that of high alumina ceramics. General properties of glasses used for substrates are shown in table VII (refs. 16 to 19 and 22), and electrical properties of various types of glasses are compared in figure 5 (ref. 20).

As sealing media, glasses perform an important role in the formation of hermetic, dielectric seals. Traditional glass-to-metal seals are formed by heating until the glass softens and bonds to a properly preoxidized metal. Seals can also be made by metalizing the surface of the glass and then joining it to the metal component with a metal solder. Low melting “solder glasses” also are used for joining various combinations of glasses (ref. 21), ceramics, or metals.

Solder glasses and their glass-ceramic modifications have provided other ways to utilize glass in microelectronics: as adhesives for joining ceramic-to-ceramic packaging, as encapsulants and sealants, as glazes for substrates, as insulators and bonds in multilayer systems, as vehicles and bonds for printed components and interconnections, and wherever the fertile imagination of designers will take them.

Glasses can be obtained in tens of thousands of compositions, and, consequently, in extremely wide ranges of properties. This
USE OF CERAMICS IN MICROELECTRONICS

(a) Temperature °C

Log ρ (ohm-cm)

Temperature 1000/°K

(b) Loss Tangent at 1 MHz

Temperature °C
Identification of Glass Codes for Fig. 5

<table>
<thead>
<tr>
<th>Type of glass</th>
<th>Corning Glass</th>
<th>Owens-Illinois</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soda lime</td>
<td>0080</td>
<td>R-6</td>
</tr>
<tr>
<td>Clear lead</td>
<td>0120</td>
<td>KG-12</td>
</tr>
<tr>
<td>Aluminosilicate</td>
<td>1723</td>
<td>EE-2</td>
</tr>
<tr>
<td>Borosilicate</td>
<td>7740</td>
<td>KG-33</td>
</tr>
<tr>
<td>High silica</td>
<td>7915</td>
<td></td>
</tr>
<tr>
<td>Fused silica</td>
<td>7940</td>
<td></td>
</tr>
<tr>
<td>Fotoceram® glass-ceramic</td>
<td>8603</td>
<td>EG-4</td>
</tr>
<tr>
<td>Capacitor</td>
<td>8871</td>
<td></td>
</tr>
<tr>
<td>Pyroceram® glass-ceramic</td>
<td>9606</td>
<td></td>
</tr>
<tr>
<td>Pyroceram® glass-ceramic</td>
<td>9608</td>
<td></td>
</tr>
</tbody>
</table>

© Trademarks of Corning Glass Works.

Figure 5.—Electrical properties of various types of commercial glasses and ceramics. (a) Relation between dc resistivity and temperature. (b) Loss tangent at 1 M as a function of temperature. (c) Dielectric breakdown at elevated temperatures. One-min breakdown for sample thickness of 2 mm at 60 cps.
**Table VII. — Properties of Glass Substrates**

<table>
<thead>
<tr>
<th>Glass code no.</th>
<th>0080 b</th>
<th>0211</th>
<th>1715</th>
<th>1723 c</th>
<th>7050</th>
<th>7940</th>
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</thead>
<tbody>
<tr>
<td>Glass type...</td>
<td>Soda lime</td>
<td>Alkali zinc borosilicate</td>
<td>Lime alumina silicate, alkali-free d</td>
<td>Lime alumina silicate, alkali-free d</td>
<td>Barium alumina silicate, alkali-free d</td>
<td>Fused silica</td>
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<td>Density, g/cc.</td>
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<td>2.63</td>
<td>2.76</td>
<td>2.20</td>
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<td>Viscosity data:</td>
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<tr>
<td>Annealing point, °C</td>
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<td>542</td>
<td>866</td>
<td>710</td>
<td>650</td>
<td>1050</td>
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<td>Softening point, °C</td>
<td>696</td>
<td>720</td>
<td>1060</td>
<td>910</td>
<td>872</td>
<td>1580</td>
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<td>Linear coefficient of thermal expansion (0°–300° C), 10⁻⁷/°C</td>
<td>92</td>
<td>72</td>
<td>35</td>
<td>46</td>
<td>45</td>
<td>5.6</td>
</tr>
<tr>
<td>Thermal conductivity (cal/cm/sec/°C):</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25° C</td>
<td>.0025</td>
<td>(e)</td>
<td>(e)</td>
<td>.0032</td>
<td>.0030</td>
<td>.0035</td>
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<tr>
<td>300° C</td>
<td>.0032</td>
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<td></td>
</tr>
<tr>
<td>Volume resistivity, log₁₀ R (Ω·cm):</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>25° C</td>
<td>12.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>250° C</td>
<td>6.4</td>
<td>8.3</td>
<td>13.6</td>
<td>14.1</td>
<td>13.5</td>
<td>11.8</td>
</tr>
<tr>
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<td>5.1</td>
<td>6.7</td>
<td>11.3</td>
<td>11.8</td>
<td>11.3</td>
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<tr>
<td>Dielectric constant, 10⁶ eps:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25° C</td>
<td>7.3</td>
<td>6.6</td>
<td>5.9</td>
<td>6.4</td>
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<td>7.4</td>
<td>6.1</td>
<td>6.5</td>
<td>5.9</td>
<td>3.9</td>
</tr>
</tbody>
</table>

* Corning Glass Works, Corning, N.Y.


* Equivalent Owens-Illinois code EE–2.

* No alkali added. Low alkali raw materials used.

* Room temperature conductivity of glasses range from 0.002 to 0.004. Conductivity increases with temperature approximately 10 percent per 100°C.
permits tailoring composition-dependent properties, such as thermal expansion, to fit the specific requirements of a particular design. Examples of solder glasses and glass-ceramics are shown in table VIII for packaging sealants and for substrate glazes and insulating films (ref. 22). In examining these tables, it can be noted that a wide variety of properties are pertinent to glazing, insulating, packaging, and sealing. These include volume resistivity, power factor, dielectric constant, thermal expansion, thermal contraction, chemical durability, density, annealing point, fiber softening point, sealing temperature and time, maximum reheat temperature, and compatibility with various ceramic-metal-alloy combinations.

Other degrees of freedom in obtaining special characteristics arise from the ease of surface modification, the sensitivity of certain properties to thermal history, the ability to homogeneously convert many glasses to polycrystalline ceramics with controllable portions of residual glassy phase, and the ability to form composite structures with metals, semiconductors, ceramics, polymers, and other glasses. Because of the viscosity-temperature characteristics of glass, it can be hot formed plastically into almost any desired shape. It can also be machined by mechanical, chemical, thermal, or radiation energy to achieve fine detail.

Until recently, glasses used for electronics were taken from the traditional formulations which had been developed for older arts and technologies. These included the soda-lime, lead oxide, borosilicate, aluminosilicate, and fused silica glasses. With the advent of microelectronics, these same types of glasses were utilized at first; but with increasing sophistication and demands for reliability, special glasses are being developed. Since the quantities required may be small for the glass manufacturer while the strategic need is important for the user in the electronics industry, a trend has developed for electronics companies and laboratories to establish their own in-house glass facilities (ref. 23).

An important consideration in utilization of glass in contact with semiconductors is the ease of migration of undesirable ions in and through glass. Alkali ions are highly mobile in glass and are undesirable contaminants for silicon devices. Solutions for this problem have included development of compositions in which alkali ions are less mobile, or special precautions to maintain alkali at only a few ppm (ref. 24).

The range of glass compositions usable for microelectronics has been limited by the requirement that the glass soften at relatively
<table>
<thead>
<tr>
<th>Article No.</th>
<th>Volume resistivity ρ (Ω-cm) expressed as logarithm of ρ at 25° C and 1 Mc</th>
<th>Power factor (Δ%) at 25° C and 1 Mc</th>
<th>Dielectric constant at 25° C and 1 Mc</th>
<th>Thermal expansion coefficient A X 10³ (annealing point to 25° C)</th>
<th>Thermal contraction coefficient b X 10³ (annealing point to 25° C) (mg/cm³)</th>
<th>Chemical durability (average weight loss of fired sealant) (30 min at 121° C)</th>
<th>Recommended sealing cycle (furnace seal)</th>
<th>Max. reheat tempd. (°C)</th>
<th>Sealable to—</th>
<th>Glasses and ceramics</th>
<th>Metals and alloys</th>
</tr>
</thead>
<tbody>
<tr>
<td>00130</td>
<td>12.4 10.5 0.50 8.2 41 60 0.05 5.27 4.07 469 571 615 ef45 550</td>
<td>EN-1 96% alumina</td>
<td>Iron-nickel-cobalt alloy: ASTM #F-15 (e.g., Kovar®, Therlo®, Rodar®) 42% nickel-iron alloy: ASTM #F-30.</td>
<td></td>
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<tr>
<td>00158</td>
<td>11.1 8.9 0.15 12.5 83 102 .62 3.10 5.38 365 441 470 ef20 425</td>
<td>KG-12, steatite, forsterite</td>
<td>Nickel-chrome-iron alloy: ASTM #F-31 (e.g., Sylvania #4, Carpenter #426) Durnet: ASTM #F-29. 52% nickel-iron alloy: ASTM #F-30.</td>
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<tr>
<td>00331</td>
<td>9.0 7.2 0.26 5.1 47 62 Negligible 2.27 482 716 740 €15 700 98% alumina</td>
<td>Iron-nickel-cobalt alloy: ASTM #F-15 (e.g., Kovar®, Therlo®, Rodar®) 42% nickel-iron alloy: ASTM #F-30.</td>
<td></td>
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<tr>
<td>00338</td>
<td>7.1 5.7 0.63 6.7 56 70 Negligible 2.32 521 710 735 €15 700 98% alumina</td>
<td>Iron-nickel-cobalt alloy: ASTM #F-15 (e.g., Kovar®, Therlo®, Rodar®) 44% and 46% nickel-iron alloy: ASTM #F-30.</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

**Package Seals**

<table>
<thead>
<tr>
<th>Article No.</th>
<th>Volume resistivity ρ (Ω-cm) expressed as logarithm of ρ at 25° C and 1 Mc</th>
<th>Power factor (Δ%) at 25° C and 1 Mc</th>
<th>Dielectric constant at 25° C and 1 Mc</th>
<th>Thermal expansion coefficient A X 10³ (annealing point to 25° C)</th>
<th>Thermal contraction coefficient b X 10³ (annealing point to 25° C) (mg/cm³)</th>
<th>Chemical durability (average weight loss of fired sealant) (30 min at 121° C)</th>
<th>Recommended sealing cycle (furnace seal)</th>
<th>Max. reheat tempd. (°C)</th>
<th>Sealable to—</th>
<th>Glasses and ceramics</th>
<th>Metals and alloys</th>
</tr>
</thead>
<tbody>
<tr>
<td>00560g³ h</td>
<td>7.6 6.4 1.5 18.5 94 98 1.71 7.13 6.48 .................. 425 60 525 KG-12, steatite, forsterite</td>
<td></td>
<td>Nickel-chrome-iron alloy: ASTM #F-31 (e.g., Sylvania #4, Carpenter #426) Durnet: ASTM #F-29. 52% nickel-iron alloy: ASTM #F-30.</td>
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</tr>
<tr>
<td>00564g³ h</td>
<td>7.8 6.4 1.3 22.8 83 89 2.33 6.66 6.3 .................. 460 60 525 KG-12, beryllia</td>
<td></td>
<td>Nickel-chrome-iron alloy: ASTM #F-31 (e.g., Sylvania #4, Carpenter #426) Durnet: ASTM #F-29. 49% and 52% nickel-iron alloy: ASTM #F-30. Platinum, Titanium.</td>
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<td></td>
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<td></td>
</tr>
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<td>Ceramic and Glass Insulators</td>
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<td>00578</td>
<td>6.8</td>
<td>5.5</td>
<td>1.8</td>
<td>24.8</td>
<td>108</td>
<td>116</td>
<td>3.57</td>
<td>2.48</td>
<td>6.49</td>
<td>380</td>
<td>60</td>
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<tr>
<td>00593</td>
<td>8.8</td>
<td>5.0</td>
<td>.96</td>
<td>27.3</td>
<td>117</td>
<td>127</td>
<td>1.14</td>
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<td>6.55</td>
<td>365</td>
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<td>80</td>
<td>2.12</td>
<td>7.60</td>
<td>6.0</td>
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<td>30</td>
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<tr>
<td>00765</td>
<td>8.5</td>
<td>6.0</td>
<td>.94</td>
<td>21.5</td>
<td>87</td>
<td>95</td>
<td>1.98</td>
<td>7.06</td>
<td>6.05</td>
<td>435</td>
<td>60</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Substrate Glazes/Insulating Films</th>
</tr>
</thead>
<tbody>
<tr>
<td>01238</td>
</tr>
<tr>
<td>01545</td>
</tr>
<tr>
<td>01756</td>
</tr>
</tbody>
</table>

- Owens-Illinois, Inc., Toledo, Ohio.
- For the crystallizing glazes and sealants, the contraction coefficient is measured from the recommended holding temperature to 25° C.
- The annealing point and the softening point apply only to the vitreous glazes and sealants.
- These temperatures can be tolerated for up to 10 min.
- The time and temperature are interrelated. Seals can be made at shorter times by elevating the temperature.

**Note:**
- These strongly absorb infrared radiation. Materials can be glazed or sealed in less than 1 min. with the appropriate source.
- These are basic materials that can either be used as supplied or modified by user. The materials to which the resulting product will seal will be determined by the properties of the modified sealant.
- Glass ceramics.
low temperatures to avoid overheating other components. Also, as successive glasses are applied for varying functions, the heat treatment temperature must be lowered each time in order to prevent disrupting previously bonded films. By the third or fourth heating, the required softening temperature can no longer be realized with a glass meeting requirements for chemical durability.

Various means to bypass this dilemma have been developed including both novel compositions and special processing techniques. In certain compositions, exceptions have been discovered to the general correlation between softening point and chemical durability (ref. 25). Entirely different families of glass composition have been explored as alternatives to the lead-zinc borates and borosilicates. These have included the extensive family of chalcogenide glasses with softening points from a few hundred degrees centigrade down to almost room temperature (ref. 26).

Another discovery has been that a glass already melted into place can have its chemical durability improved by diffusion of certain ions into it. One example is the diffusion of phosphorus into a silicate glass to form a phosphosilicate (ref. 27). Still another technique is the crystallization of one or more of the earlier glass layers to a glass-ceramic. This may not only improve the electrical and bonding properties but also raise the deformation temperature by several hundred degrees subsequent to initial bonding. Using this technique, it is feasible to heat-treat the next glassy component without dropping temperature. (The innovative techniques in applying glassy coatings to semiconductors and for crossovers will be discussed in ch. 5.)

JOINING

Joining is a critical operation wherever an electric current is being used because the conduction must often be accompanied by other functions, such as environmental isolation and electrical insulation. Combining these diverse functions in one structure is difficult and requires good engineering design and maximum application of available materials. Joining may be defined as the bringing together of the same or of different materials to form a composite unit. Composites may be laminar, or dispersed, particulate mixtures. In any case, the bond between the differing compositions and shapes may be mechanical or chemical.

The first Edison lamps required a metallic conductor, a carbon-resistor illuminating element, an insulating envelope of glass, and an insulator base through which the lead wires were introduced.
Each area where the dissimilar materials were in contact required appropriate techniques of joining. Vacuum-tube technology adapted materials and techniques from lampmaking and added additional complexities in functions and derived materials, thereby requiring further advances in designs, materials, and joining techniques. With the development of ceramic vacuum tubes, new techniques for joining had to be developed. The special techniques then developed for metalizing, soldering, brazing, welding, and sealing were later taken over for the packaging of semiconductor devices.

In microelectronics technology, all of these materials and techniques are available for use, in addition to the many others which have been specially developed. The requirements for joining techniques have become more complex, and it has become even more necessary that joining technology be based on understanding of fundamental principles and mechanisms. The functions of joining are highly diverse in microelectronics, including metalizing, enclosing, packaging, encapsulation, passivation, coating, compositing, etc.

The joining of ceramics to other materials has been surveyed and a number of other reviews of the technology have been published recently (ref. 8). A NASA Technology Utilization report has been prepared on joining ceramics and graphite to other materials (ref. 28). A recent literature survey on metal-to-ceramic seals for thermionic converters has been compiled at NASA's Jet Propulsion Laboratory (ref. 29). As a result, the consideration of joining will be limited to the materials and techniques pertinent to current microcircuitry and will be described in chapter 5.

**NASA CONTRIBUTIONS**

NASA has made many contributions to the technology of insulators in electronics, since its missions have taxed the capabilities of available materials and required extensions of their properties. Many of these contributions were concerned with film technology and will be described in chapter 5.

In 1963, NASA sponsored a program at National Beryllia Corp. to develop techniques for the growth of single crystals suitable for microelectronics applications and the precise determination of their mechanical, thermal, and dielectric properties (ref. 30). Single crystals of beryllia were grown by the water vapor transport technique, evaporation condensation, and by crystallization from melts. Sizes up to 0.175-in. diameter with average diameter of 0.050 to 0.060 in. of hexagonal-shaped platelets of mono-
crystalline beryllia were grown, mainly by the water transport method. The chemical purity of the crystals was high, with most of the impurities concentrated at the surfaces. High purity was also achieved for single crystals made by the evaporation condensation and molten salt methods. Properties were measured and correlated to the crystal structure of BeO.

An extension of vacuum-tube technology termed “integrated vacuum circuits” (IVC) has been developed at Stanford Research Institute with partial NASA support (refs. 31 and 32). In the IVC, large numbers of coplanar diodes and triodes are formed on a single disk of sapphire by photolithographic means. A strip of tungsten oxide is used as the thermionic-emission cathode, while strips of titanium are used as grid and anode. The entire circuit, including interconnections, is part of an evacuated package, and the entire substrate is heated to raise the cathode to emitting temperature.

Devices of this type are able to withstand extreme environments of ambient temperature, up to 600° C; high nuclear radiation, $10^8$ more neutrons and $10^3$ more gamma rays total dosage before failure than radiation-hardened semiconductors; and severe electromagnetic radiation. Possible applications include high-heat environments of geophysical exploration, wing instrumentation for the supersonic transport, nuclear instrumentation, and nuclear guidance systems.

Lewis Research Center performs research on engines and power systems for interplanetary travel (ref. 33). This work has required developing unique materials that show exceptional electrical characteristics. There has been considerable interest in improved high dielectric strength coatings on metals and materials for high-voltage, high-temperature applications. While most of this work is not directly concerned with microelectronics, many developments are beyond the level of commercially available materials. Microelectronics research personnel should be aware of the work at Lewis in order to relate it to their problems.

A study of the high-temperature electrical properties of insulators and their compatibility with refractory metals was sponsored by NASA at the IIT Research Institute (refs. 34 to 36). Electrical resistivity as a function of temperature and time in various atmospheres was measured, and the change in physical properties of refractory metals in contact with ceramics was determined. The ceramics tested were alumina (polycrystalline

*A naturally occurring ceramic readily machined and fired to achieve stable properties (American Lava Corp.).
and sapphire), magnesia, boron nitride (hot pressed and pyrolytic), thoria, beryllia, lava,² boron nitride-carbon alloy, and lime-stabilized zirconia. The atmospheres were vacuum, nitrogen, hydrogen, ammonia, methane, water vapor, and vapors of cesium and mercury. Refractory metals and alloys included tungsten, tantalum, 90 Ta–10 W alloy, molybdenum, and TZM (Mo–0.5 Ti–0.08 Zr) alloy. All of these materials were of the highest purities available.

Electrical measurements were normally made at voltages up to 90 V dc, although 500 and 1000 V dc were also used. Temperatures of measurement were between 800° and 1850° C. The ceramics displaying the best properties were alumina, magnesia, beryllia, and boron nitride. For these ceramics it was found that the electrical resistivity of the insulators was, in general, only slightly affected by the test atmosphere. Long-term tests on alumina, beryllia, and boron nitride showed that resistivity increased with time, indicating removal of charge carriers by ionic migration.

Alumina appeared to be slightly more compatible with metals than magnesia and, on short-term tests, the metal samples were little affected by contact with beryllia. Boron nitride reacted with all metal specimens. Tungsten and molybdenum could be heated in contact with ceramics under hydrogen and nitrogen without harmful effects, but TZM, tantalum and 90 Ta–10 W alloy were embrittled to varying degrees under these atmospheres.

Research continuing in the field of high-temperature, high-purity, high-resistivity materials includes projects to develop (1) a protective sleeve to shield the stator of an alternator from potassium vapor at high temperatures, (2) a thermionic diode design utilizing beryllia for application at 1200° C for 43 000 hr, (3) thermocouple insulation at 1800 to 2000° C. If the emf of the thermocouple degrades, the relationship at which it changes must be known. In addition, work has been done on developing high-temperature thyatron units utilizing highly corrosive thallium and cesium vapors (refs. 37 and 38).

In research at Lewis Research Center on a thermionic diode, a high-temperature cermet seal was developed with both high electrical resistivity and high thermal conductivity (ref. 39). Thermionic diodes convert heat directly into electrical energy. They do this by utilizing the Edison effect in which electrons are emitted from a heated metal. The schematic of a simple thermionic diode (ref. 40) is shown in figure-6. The heated cathode emits electrons which the cooled collector gathers and feeds to a load.
The circuit is completed by electrically connecting the load to the emitter. Efficiency of the thermionic diode is aided by bringing the collector close to the emitter and introducing positive ions, such as cesium, into the space between the two electrodes. Both of these design features place stringent requirements on the insulators that must separate the two electrodes. Ideally, the insulator must maintain hermetic seal, have adequate electrical resistance at operating temperature, be resistant to cesium attack, have good structural integrity at high temperatures, and have good thermal conductivity. Seals utilizing ordinary ceramics satisfied all requirements except that of thermal conductivity.

The seal developed has one or more layers of alumina-coated niobium particles sandwiched between thick niobium pieces and bonded by isostatic hot pressing. The hermetic seal has resistivity greater than 5 mΩ at 1000° C, structural integrity to 1400° C, and excellent thermal shock resistance to 1200° C. The seal has an initial tensile strength of 25 000 psi, and still tolerates 13 000 psi after cycling several times to 1400° C. Thermal conductivity is about 0.6 that of metallic niobium.

A cross-sectional view of a typical graded seal is shown in figure 7. The seal is prepared by assembling layers of niobium and alumina-coated niobium powders of various alumina/niobium ratios. In the seal shown the layers were: niobium; 80 vol % niobium–20 vol % alumina; 50 vol % niobium–50 vol % alumina; 80 vol % niobium–20 vol % alumina; and niobium. The niobium powders were 50 μm in diameter and the alumina of 99.5 percent
CERAMIC AND GLASS INSULATORS

Figure 7.—Cross-sectional view of a graded niobium-alumina coated niobium particle seal.

Purity was deposited onto niobium particles through a fluidized bed. The assembled seal was contained within a sealed niobium can and isostatically hot pressed at 3000°F under 20,000 psi for 2 hr. A plot of the resistivity of the seal as a function of temperature is shown in figure 8, in comparison with resistivity data for a different graded seal design utilizing a Lucalox® ceramic center, Lucalox ceramics, and alumina ceramic. The composite described has high resistivity and good thermal conductivity. It is used for power tube grids and other high-power tube applications. The materials can be easily sawed or machined and can be brazed.

In constructing a Kaufman-type electron-bombardment thruster at Lewis Research Center for interplanetary travel, it was advantageous to replace a screen grid by an insulator contiguous to an accelerator grid (refs. 41 and 42). A schematic of the original double-grid design and of the glass-coated single-grid design is shown in figure 9 and a sectional view of a Kaufman ion thruster in figure 10. Requirements of the coating were

1. Complete adhesion to the molybdenum grid with no laminate
2. No bubbles or other defects that would reduce the dielectric strength

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(3) Conformability without bridging of grid openings
(4) Practical application to a 30-cm-diameter grid with 0.2-cm-diameter holes, 50 percent open area, and 0.04-cm-thick molybdenum

It was found possible to apply Corning 7052 glass in nearly bubble-free coatings using conveniently available processes, temperatures, and heating times. To do this, however, it was necessary to develop a "helium diffusion process" that eliminated bubbles formed in normal firing operations utilizing a neutral atmosphere other than helium. The preparation process was also theoretically analyzed to optimize glass-coating thickness and to control the helium diffusion.

Preparation of the coating consisted of cleaning and deburring the grid, oxidizing the grid at 538° C for 5–10 min, removing the oxidized layer from the downstream side, applying a slurry of water plus powdered glass, and drying. The grid was then fired, coating side up, in a helium atmosphere for 5 min at 1444° C and then for 15 min in argon at the same temperature. The helium atmosphere served the purpose of protecting the molybdenum grid
Figure 9.—Accelerator grid systems. (a) Conventional double-grid system. (b) Fused glass composite accelerator grid.
from oxidation, and helium gas trapped in pores in the glass coating diffused rapidly out of the coating during the argon atmosphere stage.

The effective dielectric strength of fused glass coatings on unperforated plates made by the diffusion process is $8.5 \times 10^7$ V/m for coatings of approximately 0.035-cm thickness. An improvement with the diffusion technique suggests the possibility of utilizing this method for other glass-coating processes to achieve bubble-free coatings.

NASA-sponsored work in material research centers includes some work on ceramic insulators and glasses. At RPI, studies were made of amorphous insulating films of silicon nitride. The effects of nonstoichiometry on properties and the relationship between the noncrystalline films and their compounds have been studied by J. D. Mackenzie. In addition, the formation of indentations on glass and the question of how glass structure and bonding can affect hardness are being examined. Included are measurements on the flow during and after indentation of silica and alkali-oxide-silica glasses (ref. 43).
Ceramics and Glasses in Resistors

The trend in electronics toward microminiaturization and integrated circuitry has brought a proliferation of materials and assembly techniques for resistive arrays. A few years ago the designer was limited by technology and costs to a narrow selection of resistive elements; innovations in materials and processing now provide many options. These include discrete resistors on printed circuit boards or designing resistors directly into integrated circuits. Film technology can be adopted, allowing resistors to be incorporated into hybrid circuits using thick or thin films, or chips. In choosing from these options, not only must the properties and relative merits of each system be analyzed, but, in addition, different compositions of resistive elements in each of the film technologies must be appraised.

The resistor industry is a large one—having sold 5 billion units at a total value of $400 million in 1968 (ref. 44). A breakdown of sales for discrete resistors according to types is as follows:

<table>
<thead>
<tr>
<th>Type of Resistor</th>
<th>Sales—Millions of Dollars</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Composition</td>
<td>69</td>
</tr>
<tr>
<td>Deposited Carbon Film</td>
<td>20</td>
</tr>
<tr>
<td>Metal Film</td>
<td>50</td>
</tr>
<tr>
<td>Wire Wound</td>
<td>50</td>
</tr>
<tr>
<td>Variable:</td>
<td></td>
</tr>
<tr>
<td>Wirewound</td>
<td>75</td>
</tr>
<tr>
<td>Nonwirewound</td>
<td>95</td>
</tr>
<tr>
<td>Multiturn</td>
<td>25</td>
</tr>
<tr>
<td>Thermistors and Varistors</td>
<td>27</td>
</tr>
</tbody>
</table>

No data were available for the resistors used in monolithic, film networks, or hybrid circuits, but these are rapidly increasing in importance. Forty percent of sales are industrial, 30 percent commercial, and 30 percent military.

DISCRETE RESISTORS

Discrete resistors for electronics are usually placed in one of three general categories (refs. 45 and 46): general purpose, pre-
cision, and power. The general-purpose resistors are used where high accuracy is not necessary. Tolerances of ±5, ±10, and ±20 percent may be acceptable. Precision resistors must be made to higher accuracies and tolerances as tight as ±0.005 percent. Between these two extremes, a wide range of tolerances and variations in other properties is available, and another category, the semiprecision, is sometimes used. Power resistors are used in applications when it is necessary to dissipate varying amounts of power—from watts for lower power uses to thousands of watts in transmitting equipment.

The categories above are satisfied by several classes of resistors which overlap. Carbon composition resistors are the original workhorse of the general-purpose category. They are being supplemented by film resistors having improved properties: deposited or cracked carbon, tin oxide, metal, and metal-glass\(^3\) types. There are also applications for wirewound resistors in this category. For precision applications, wirewound resistors offer a combination of desirable properties. However, metal-film and tin oxide resistors are replacing wirewounds in many applications and, for semiprecision use, film resistors of all types compete with wirewound types. For power applications, wirewound resistors are the standard, but tin oxide and metal-glass resistors also have portions of this market.

In choosing a resistor for a particular purpose, these criteria apply: (1) size, (2) power handling capability, (3) stability, (4) accuracy, (5) maximum operating temperature, (6) maximum operating voltage, (7) frequency range, (8) noise, (9) temperature coefficient of resistance (TCR), (10) voltage coefficient of resistance (VCR), (11) reliability, (12) performance under high humidity, (13) shelf life, and (14) load life. A summary of properties for the six types mentioned is shown in table IX.

**Carbon Composition Resistors**

Carbon composition resistors are made in one of two types: molded or film. The molded carbon composition resistors have been used in large numbers since circuit designers know they will perform reliably in a majority of applications. In many cases today, designers are specifying more expensive and less-proved components in applications where a molded carbon composition resistor would perform as well. Custom resistors are made by mixing the raw materials, consisting of carbon black, resin binder,

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\(^3\)Metal-glass thick-film resistors are also called cermet or metal-glaze resistors.
<table>
<thead>
<tr>
<th>Property</th>
<th>Carbon composition</th>
<th>Deposited carbon film</th>
<th>Tin oxide</th>
<th>Wire-wound</th>
<th>Metal film</th>
<th>Metal glass, cermet, or metal glaze</th>
</tr>
</thead>
<tbody>
<tr>
<td>Principal application</td>
<td>General purpose</td>
<td>General purpose</td>
<td>Precision and general purpose</td>
<td>Precision</td>
<td>Precision</td>
<td>General purpose</td>
</tr>
<tr>
<td>Range in resistance value, Ω</td>
<td>1–22 M</td>
<td>10–50 M</td>
<td>10–66 M</td>
<td>0.1–1 M</td>
<td>10–500 K</td>
<td>10–10 M</td>
</tr>
<tr>
<td>TCR, ppm/°C</td>
<td>±1200</td>
<td>−150 to −500</td>
<td>±50</td>
<td>±25</td>
<td>±25</td>
<td>&lt;100</td>
</tr>
<tr>
<td>Noise</td>
<td>Poor</td>
<td>Fair</td>
<td>Good</td>
<td>Excellent</td>
<td>Good</td>
<td>Fair</td>
</tr>
<tr>
<td>Service stability</td>
<td>Poor</td>
<td>Fair</td>
<td>Excellent</td>
<td>Excellent</td>
<td>Excellent</td>
<td>Good</td>
</tr>
<tr>
<td>Resistance to catastrophic failure</td>
<td>Excellent</td>
<td>Fair</td>
<td>Excellent</td>
<td>Good</td>
<td>Fair</td>
<td>Good</td>
</tr>
<tr>
<td>VCR, ppm/V</td>
<td>Poor</td>
<td>Fair</td>
<td>Good</td>
<td>Excellent</td>
<td>Good</td>
<td>Fair</td>
</tr>
<tr>
<td>Power range:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Smallest, W</td>
<td>1/8</td>
<td>1/8</td>
<td>1/20</td>
<td>1/8</td>
<td>1/20</td>
<td>1/4</td>
</tr>
<tr>
<td>Largest, W</td>
<td>2</td>
<td>2</td>
<td>&gt;10</td>
<td>&gt;10</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Frequency response:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low frequency</td>
<td>Good</td>
<td>Good</td>
<td>Good</td>
<td>Good</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>High frequency</td>
<td>Fair</td>
<td>Fair</td>
<td>Good</td>
<td>Poor</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>Property</td>
<td>Carbon composition</td>
<td>Deposited carbon film</td>
<td>Tin oxide</td>
<td>Wire-wound</td>
<td>Metal film</td>
<td>Metal glass, cermet, or metal glaze</td>
</tr>
<tr>
<td>--------------------------------</td>
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<td>-----------------------</td>
<td>-----------</td>
<td>------------</td>
<td>------------</td>
<td>-------------------------------------</td>
</tr>
<tr>
<td>Shelf life, yr.</td>
<td>Good</td>
<td>Good</td>
<td>Good</td>
<td>Good</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>Form:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Discrete (axial lead)</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Discrete (chip)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Integrated, 2-dimensional network</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Design flexibility</td>
<td>Limited</td>
<td>Limited</td>
<td>Limited</td>
<td>Limited</td>
<td>Good a</td>
<td>High b</td>
</tr>
<tr>
<td>Material type:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Composite</td>
<td>Carbon black and resin</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Conductor and glass</td>
</tr>
<tr>
<td>Homogeneous</td>
<td>Carbon</td>
<td>SnO₂ + Sb₂O₃</td>
<td>Nickel-chromium alloys</td>
<td>Nickel-chromium alloys</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Relative cost</td>
<td>Low</td>
<td>Intermediate</td>
<td>Intermediate</td>
<td>High</td>
<td>High</td>
<td>Intermediate</td>
</tr>
</tbody>
</table>

X = Indicates availability.

a Based on photoetch work technique.

b Based on screen-printing technique.
and refractory filling in the proper proportions, compressing the resultant black powder into a cylindrical shape, and curing in a furnace which solidifies the slug. End connections are made by molding the enlarged ends of the connecting wires directly into the ends of the carbon rod. The finished resistor can be either uninsulated or insulated with an organic encapsulant. An automatic testing and sorting process is used to classify the resistors by measured resistance values. The resistors are then color coded.

A second type of molded carbon composition resistor is made with ceramic insulation. An extruded rod of resistor material is cut to the desired length and cured. The rods are then placed in ceramic tubes, and brass caps placed over copper-sprayed ends. The ends are then sealed with a moisture-resistant cement. As with the molded carbon composition resistors, testing, sorting, and color coding are automatic.

Carbon composition film-type resistors are made by drawing a continuous tube of glass through a liquid mixture of carbon black, resin binder, and refractory filling, with subsequent curing. With this process it is possible to monitor the resistance of the coating and adjust resistance by changing the resin or compositions. The coated filament is cut into desired lengths and contoured leads are inserted into the ends of the tubes. Permanent electrical connections are made by a conducting adhesive that joins the lead to the film. After curing the adhesive, the assemblies are molded in a thermostetting plastic jacket and color coded.

**Discrete Film Resistors**

Film resistors are a result of attempts to fulfill the need for resistors showing better properties than carbon composition types and less bulkiness and cost than wirewound types. The first successful resistor of the film type was the *deposited carbon resistor* (ref. 47). It is made by placing a ceramic rod in a vessel filled with a hydrocarbon gas and an inert gas and heating until a carbon film is deposited on the ceramic core by a gas-cracking process. By varying the gas mixture, the temperature of the process and the time of deposition, films of varying thicknesses and properties may be produced. Final resistance is determined by a helical pattern machined into the deposited film. This can be done automatically and the resistance can be monitored during the operation. Final handling is similar to that of the carbon composition film types, but the deposited carbon resistors are usually coated rather than molded in a resin.
The required properties of the ceramic core for deposited carbon film resistors and a description of their composition and manufacture have been given by Rigterink (ref. 48). Required properties are:

1. Low dielectric loss
2. High dc resistivity
3. Good thermal shock resistance
4. Imperviousness to gases to avoid carbon in pores
5. Adherent surface characteristics
6. Fine surface finish and absence of surface pinholes, cracks, iron spots, overfluxed areas, scratches, die marks, and other imperfections

An alkaline earth porcelain was found to be suitable after examining various types of available ceramics, including steatite and zircon porcelains. The surface of the fired ceramic was found to be fine-grained mullite ($3\text{Al}_2\text{O}_3\cdot\text{2SiO}_2$) crystals no longer than 4 μm dispersed in a glassy phase. This surface was found to be close to ideal as a substrate for thin carbon films.

Deposited carbon resistors have greater stability and closer tolerances than carbon composition resistors. A 1-percent tolerance is standard and 2 percent in higher resistance ranges, although many are sold to a 5-percent tolerance. Many values can be obtained at 0.5 percent. Deposited carbon resistors have lower levels of current noise and their VCR is also better than the carbon composition type. Wattage sizes available are $1/8$, $1/4$, $1/2$, 1, and 2, and the resistance range is 10 Ω to 10 MΩ (ref. 49).

Metal film resistors are an improvement over deposited carbon resistors because they are more precise and stable. The metal film resistor has extremely low noise and TCR as well as high stability. As in the case of the deposited carbon resistor, the metal-film resistors are deposited onto a ceramic substrate, terminated, helixed, capped, and coated or molded for protection. A cutaway view of a metal-film resistor revealing construction features is shown in figure 11 (ref. 50).

The structure of the evaporated metal film has been shown to be not metal alone, but a complicated mixture of metal and metal oxide. The properties of films with high resistivities and negative TCR's are generally attributed to a lack of continuity between the metallic grains of which the film is composed. As a result, the electrical properties of the metal alone do not determine characteristics, and behavior has been explained in terms of quantum-mechanical tunneling between grains. TCR's from 25 to 250 ppm/°C are available and wattages from 1/10 to 2 W.
range of resistances from 10 Ω to 10 MΩ is available. An extremely high reliability is claimed for this type of resistor with a failure rate not exceeding 0.0004 percent per 1000 hr at the 60-percent confidence level, where a change in resistance of 0.5 percent constitutes a failure (ref. 51).

Tin oxide film resistors are another improvement over the carbon composition resistors in that they can be made to closer tolerances and with greater stability, meeting metal-film electrical parameters as well. Resistors of this type are classified as precision, semiprecision, and general purpose. According to the grade selected, their TCR's are ±50 to ±220 ppm/°C from −55° to +175° C. Voltage ratings are from 200 to 750 V depending on design. Their power ratings range from 1/20 to 2 W. In power designs they range from 2 up to 6000 W in a special air-cooled design. For the power resistors, voltage ratings go from 500 V to 72 kV and TCR's are ±200 ppm/°C for units too low and ±500 ppm/°C for units above 10 W.

The tin oxide resistors are made by a continuous process in which films of antimony-doped tin oxide are deposited onto hot glass rods, resulting in a film chemically bonded to the glass substrate. The basic reaction involves the conversion of tin tetrachloride to tin oxide by hydrolysis. During the process the glass is heated close to its softening point (approximately 650° C), and a chemical reaction takes place on the glass surface as it passes through the furnace atmosphere containing the tin tetrachloride.
vapors. The thermal expansion of the tin oxide films is matched to that of the substrate, which minimizes stresses. Antimony oxide additions improve uniformity of deposition, reproducibility, range of resistance, and TCR. Adherence to the substrate, film resistivity, TCR, as well as other properties of the resistor are controlled during the deposition. To achieve the desired resistance, a path is formed by cutting a spiral along the glass core (refs. 47 and 52). A silver-glass composition is fired onto the element for the electrical connection to the tin oxide film. Metal end-cap and lead assemblies are press fitted to provide for a secure mechanical and electrical connection. After application of end caps and leads, the resistors are coated with an encapsulant and color coded or type marked. One series utilizes an inorganic coating to provide a flameproof part for critical applications.

A relatively new item is the metal-glass resistor which is similar in structure to the thick-film resistors described later in this chapter. These resistors are bonded to ceramic substrates. The earliest ones available were based upon noble metals in combination with borosilicate glazes. The greater thickness of the glass relative to thin films and the use of a relatively high thermal conductivity alumina core give this resistor ruggedness and a high power capability. Recently, resistors using nonnoble metals and metal compounds have come into use. It has been found that metals such as titanium, chromium, zirconium, molybdenum, tantalum, and tungsten when used in conjunction with the borides, carbides, nitrides, oxides, silicates, and phosphides of these metals produce useful metal-glass materials (refs. 47, 53, and 54). TCR’s of 200 ppm/°C or less, ruggedness, resistance to chemical attack, good stability against voltage and temperature stresses, and insensitivity to moisture have been achieved with these resistive films. Sheet resistivities of 0.1 Ω/sq to several thousand Ω/sq have been produced. Resistors from the tungsten carbide-tungsten glaze system in the ¼-W size can be operated at 1 W at room temperature or at ½ W at 70° C with no greater change in load life than that experienced at ¼ W. This system has a TCR of ±200 ppm, can be purchased with an initial tolerance of ±2 percent, can be used as a 4-percent end-of-life tolerance design, and exhibits changes in resistance under 1 percent on all environmental testing.

**Wirewound Resistors**

Wirewound resistors offer the greatest stability and precision. Stability exceeds that of the metal-film types, VCR is practically zero, and TCR is 5 ppm/°C over 50 Ω and 10 to 20 ppm/°C under
Resistance values range from 0.1 Ω to 5 MΩ in tolerances of 0.01 to 1 percent for wattages of 1/10 to 2½. Besides being available as the precision type described above, wirewound resistors are available for general-purpose and power applications. The general-purpose resistors are made in a range from 0.24 Ω to 1500 Ω, tolerances of 5, 10, and 20 percent and powers of ½, 1, and 3 W. Power wirewound resistors are available in fixed and variable resistance styles from 2 to 250 W and 2 to 20 percent tolerances. A disadvantage of wirewound resistors is their inductance. This can be minimized by bifilar winding, but at higher frequencies the inductance can still be considerable (ref. 51).

The resistance wire used in wirewound resistors is usually an alloy to optimize desirable properties which may best be achieved in a specially formulated metal. Properties which may be controlled include TCR to as low as ±0.15 ppm/°C over a wide range of temperature, resistivity values from that of silver to practically 100 times that of copper, corrosion resistance, handling properties, and compatibility with vitreous enamels and substrates. The most commonly used resistance wires are nickel based, or copper based, although precious-metal compositions have also been used. The resistivity of the wire is selected so that adequate turns are available for controlling the final value of the resistor. Automatic feeding and winding of the wire requires accurate control of tension so as not to stretch the wire. Wire thicknesses as small as 0.0005 in. are possible (ref. 46).

In precision resistors a high-grade ceramic, on a molded or machined epoxy, is used for a core; general-purpose and power wirewound resistors may have a ceramic or a fiber-glass core. The requirements for the ceramic cores are similar to those of the deposited-carbon cores with the exception of a lack of need for a fine surface finish. For the power resistors, when high operating temperatures up to 350°C are anticipated, ceramic cores and vitreous enamel coatings protect the wire from oxidation. Beryllium oxide ceramic materials are also used extensively for power resistors which are operated at high power densities.

**Chip Resistors**

The development of thick- and thin-film hybrids, instead of all-integrated circuits, or all-film circuits, has led to the introduction of chip components. These offer electrical characteristics not currently available in circuits made by just one technology. Figure 12 shows typical resistor chips currently available commercially (ref. 55). These chips are only 0.05 by 0.05 by 0.01 in. in
FIGURE 12.—(a) Resistor chips. (b) A schematic showing the circuitry, and a gold platinum alloy surface film useful for bonding to substrates, and general specifications.
size and offer the designer a choice in his hybrid resistive circuit designs.

Chip resistors, consisting of metal-glass resistive films on 96% $\text{Al}_2\text{O}_3$ substrates, 0.05 by 0.05 by 0.012 in., are also available. The contacts are either a weldable gold formulation or a palladium silver alloy. Resistance range is 100 $\Omega$ to 15 M$\Omega$, tolerance is $\pm 10$, $\pm 5$, or $\pm 1$ percent, power dissipation is 1/10 W, and TCR is 150 ppm/°C from $-55$ to $+155$° C. Contacts can be made by soldering either directly or by reflow techniques. Mounts can be epoxy with wire leads welded to gold terminals.

A third design of metal-glass chip resistors has a rectangular box shape of 0.080 by 0.060 by 0.027 in. (ref. 56). The ends of the 0.060- by 0.027-in. sides are electroded and overlap by 0.012 in. onto the 0.080- by 0.027-in. and 0.080- by 0.060-in. sides. The chips may be mounted in a variety of ways. Resistance range is from 0.2 to 22 M$\Omega$; tolerances available are $\pm 5$, $\pm 10$, and $\pm 20$ percent; power rating is 1/20 W; and TCR is normally $\pm 200$ ppm/°C from $-55$ to $+150$° C, but can be supplied at $\pm 100$ ppm/°C.

**Special Resistors**

There are many types of special resistors, such as:

1. **High-value resistors**: Used to detect minute currents (refs. 45 and 46).
2. **High-voltage resistors**: Used where high voltages require a special construction (ref. 45).
3. **Microwave resistors**: Used where high frequencies introduce special problems (ref. 45).
4. **High-temperature resistors**: Used for abnormally high temperatures (ref. 45).
5. **Thermistors**: Based upon semiconducting oxides or carbides whose electrical resistance varies markedly with the temperature. This important characteristic enables thermistors to perform many unique regulatory functions. The NTC type has a negative temperature coefficient of resistance (refs. 45, 46, 57, and 58), while the PTC has a positive temperature coefficient of resistance (ref. 59).
6. **Varistors**: Based on semiconducting oxides or carbides that have extremely nonlinear voltage-current behavior, with current increasing as an exponential function of the voltage. This behavior makes the varistor useful for protection of voltage-sensitive components. By connecting a varistor across such a component or to ground, harmful voltage peaks may be shunted (ref. 58).
Variable resistors: Resistors that can be changed in value by simple mechanical adjustment. Variable resistors can be of wirewound, metal-film or metal-glass construction. Resistance is changed by a movable control that shortens or lengthens the resistive path.

FILM RESISTORS FOR MICROELECTRONICS

Although the distinctions between thin and thick films have often been vague, the definitions becoming accepted are based upon the methods by which the films are prepared and not necessarily their “thickness.” Thick films are characterized by preparation from fine powders, normally applied to ceramic substrates by techniques such as screen printing, spraying, or doctor blading. Thin films are prepared by a vapor technique such as vacuum evaporation, chemical vapor deposition, sputtering, etc. While thin films are usually “thinner” than those prepared by printing techniques, there is an overlap, with thin films ranging from 10 to 10⁶ Å and thick films from 1000 to 10⁶ Å (3 mils).

For resistors the question whether to use thick or thin films remains in part unanswered, and contributes to a continuing dialog in microelectronics. However, the designer can make a choice of specific devices and circuits depending upon the particular market and economic factors. In the last few years, there has been a major upsurge in the use of thick-film components, owing to a greater understanding of the mechanisms involved in processing, the availability of better properties through the development of metal-glass materials, and the ability to combine various passive components. Less capital investment, less maintenance, and less skilled labor and supervision have also been factors. Thick films utilize techniques familiar to most materials specialists, while thin films have required supervision by highly specialized physicists and more sophisticated high-vacuum engineering.

Generally speaking, thin-film resistors display greater stability than thick-film types, although this is almost always due to a lower power-loading density. For many thick-film metal-glass resistors, stability at equivalent power levels will be better than that of thin-film resistors. In high-resistance applications, thin films require a large substrate surface area and may have film discontinuities due to the method of formation. Thick-film resistors, although less precise, are currently put to a large number of diversified uses, especially for nonmilitary markets. This is partly because of miniaturization advances in thick-film network designs and ability to adjust resistor values by automated, highly
efficient processes. For instance, thick-film resistor networks are now being produced in packages of 0.050- by 0.250- by 0.375-in. dimensions. Thick films are also competing in applications for networks which require close reproducibility between resistor elements over a temperature range (tracking). In such cases a TCR stability of 5 ppm/yr can be obtained at a lower cost with thick than with thin films. A comparison of the range of properties available in representative thick films and thin films is given in Table X (ref. 60), and a discussion of each type follows.

Thick- and thin-film resistance values are often expressed as sheet resistivities in Ω/sq. Its significance can be understood from the equations shown below:

\[
\text{Resistance } R = \frac{\rho L}{A}
\]

where
\[
\rho = \text{bulk resistivity}
\]
\[
L = \text{length}
\]
\[
A = \text{area}
\]
or

<table>
<thead>
<tr>
<th>Table X.—Film Resistor Types</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrical</td>
</tr>
<tr>
<td>Tolerance</td>
</tr>
<tr>
<td>Stability, long term</td>
</tr>
<tr>
<td>Temperature coefficient</td>
</tr>
<tr>
<td>Tracking</td>
</tr>
<tr>
<td>Sheet resistivity</td>
</tr>
<tr>
<td>Resistance</td>
</tr>
<tr>
<td>Noise</td>
</tr>
<tr>
<td>Voltage coefficient</td>
</tr>
<tr>
<td>Power-handling capability</td>
</tr>
<tr>
<td>Overall design, tolerance</td>
</tr>
<tr>
<td>Film thickness</td>
</tr>
<tr>
<td>Process</td>
</tr>
<tr>
<td>Materials</td>
</tr>
<tr>
<td>Equipment</td>
</tr>
<tr>
<td>Equipment cost</td>
</tr>
<tr>
<td>Handling of finished substrate</td>
</tr>
<tr>
<td>Minimum line/space width</td>
</tr>
</tbody>
</table>
\[ R = \frac{\rho L}{tw} \]

where

- \( t \) = thickness of resistor film
- \( w \) = width of film

The sheet resistivity \( \rho_s \) in \( \Omega/\text{sq} \) per mil thickness is

\[ \rho_s = \frac{\rho}{t} \]

\[ R = \rho_s \frac{L}{w} \]

since

\[ \frac{L}{w} = \frac{\text{length}}{\text{width}} = \text{number of squares} \]

For instance, if a film resistor of length \( L = 0.060 \) in., and width \( w = 0.030 \) in. has a sheet resistivity \( \rho_s \) of 1000 \( \Omega/\text{sq} \), its resistance \( R = 1000 \times 60/30 = 2000 \Omega \).

**Thick-Film Resistors**

A large effort over the last 10 years has been expended on the development of thick-film resistors. The most useful type is the metal-glass combination, although this type was preceded by carbon-film resistors. Carbon-film resistors are a mixture of carbon particles in a polymeric binder and are comparable to discrete carbon composition resistors. Ease of manufacture and low cost are their principal advantages. Limitations in overall properties and reliability have restricted their use. Metal-film resistors consist of a thin (1000 Å) precious-metal film sandwiched between two layers of insulating glass. Because they are true metal films, their advantages are similar to wirewound resistors: low noise and availability in low-resistance ranges. Their principal disadvantages are unavailability of high resistances and a large TCR due to expansion mismatch with the ceramic or glass substrate (ref. 60). Glass-metal resistors consist of a mixture of precious metals and/or precious metal oxides and glass. They can be designed to be compatible with glass or ceramic substrates and sustain substantial overloads. They offer a wide range of desirable properties, including low cost and high reliability. Various types of metal-glass systems are described in the following sections.

**Silver-Palladium/Palladium Oxide Systems**

Early work in thick-film resistors was conducted by D’Andrea (ref. 61), and the first commercially successful system was reported by Hoffman (ref. 62) and by Casey et al. (ref. 63). This
system was based on a combination of palladium and silver with a glass frit (lead and/or other bivalent oxide borosilicates). Upon firing in air, some palladium oxide formed to serve as a bridge between the metal and the glassy oxide bond. Such a bridge leads to a gradual change in resistivity with composition in place of the usual abrupt change in resistance exhibited by mechanical mixtures of metal and insulators. Continued patent activity in this system has been evident (refs. 64 and 65). For example, substitution of the noble metal oxide for the metal is claimed to make the resistive glaze less dependent on firing conditions and also to provide reduction of the TCR. From the original basic patents, much R&D has been carried out on the silver-palladium/palladium oxide resistor system.

There are two general approaches to the preparation of thick-film resistors involving a glass metal, namely the dynamic (firing dependent) and static (firing independent) systems. In the first, the compounds are formed by reactions in situ on the substrate. In the static system, the compounds are prereacted, then made into a slurry or paste, applied to a substrate, and fired at a lower temperature to sinter the composite film.

Examples of static and dynamic resistor systems are found in Du Pont 7800 and 8000 series, palladium-based resistor compositions. The 7800 series is a static system and can be described as:

\[
PdO + Pd + Ag + \text{glass} \xrightarrow{\text{heat}} PdO + PdAg + \text{glass}
\]

In the dynamic 8000-series composition, the Pd is oxidized during firing:

\[
Pd + Ag + \text{glass} \xrightarrow{\text{heat}} Pd + PdO + PdAg + \text{glass}
\]

The advantage of a static system is its lack of dependence on the firing cycle. This is desirable during production based upon the temperature profile remaining constant.

A limitation of the static system is the dependence of the sheet resistivity upon many electrical parameters, such as TCR and VCR, current noise, and frequency response. This makes it difficult to use materials having a wide range of sheet resistivity on the same substrate, particularly where low TCR and close temperature tracking are required.

In the case of a dynamic system, the electrical properties are strictly dependent on firing time and temperature cycle. By using a constant resistor composition and firing temperature, but by varying the firing time, it is possible to obtain screened re-
sistors with different sheet resistivities and TCR. In the case of palladium-glass resistors, it has been found experimentally that the electrical properties of resistors depend on the sheet resistivity and are not strictly dependent on the firing method used to bring the material to the prescribed ohmic value. For example, a $10^4\Omega$-sq composition was found to have similar electrical characteristics, whether fired for 1 min at 750° C, for 10 min at 700° C, or for 60 min at 650° C.

Du Pont has recently marketed a new series of resistive metal-glass pastes called Birox. At the time of this writing the composition had not been disclosed. Besides offering improvements in properties, the new series has a much finer microstructure, which suggests using the films for variable resistors where low-friction sliding contacts are desirable. Performance characteristics of the Du Pont cermet pastes as well as systems based on ruthenium oxide and thallium oxide are shown in table XI.

**Ruthenium Oxide System**

Early work on the ruthenium oxide-glass resistive system was done by Faber et al. (ref. 66) and Daily et al. (ref. 67). Composition details on resistor glazes for this system were reported by Iles (ref. 68). This system has an extremely wide range of resistivity values as a function of ruthenium dioxide/glass ratio. Ruthenium oxide is normally partially defective in oxygen, probably with a corresponding amount of $^{3+}$Ru in place of $^{4+}$Ru in the crystal lattice. A “doping” technique in which a $^5+$ ion such as $^5+$Nb is added to the ruthenium dioxide provides a means of controlling the sheet resistivity and TCR over a wide range of values.

**Thallium Oxide System**

The thallium oxide-glass resistive system has been developed by F. M. Collins and his colleagues at Airco Speer Research & Development Laboratories. A portion of this work was sponsored by NASA. Unique characteristics of the system include a wide range of sheet resistivities, a relatively low firing temperature, insensitivity to furnace atmosphere, uniformity and reproducibility, and a low, linear TCR (refs. 69, 70, and 71).

The thallium oxide system was advanced as a low-cost thick-film system superior to carbon composition films and one with production advantages. Collins reported that the thallium oxide system is the only commercial thick-film resistor paste that does not use precious metals. Advantages are said to be that it can be fired at lower temperatures, that it can be cofired with silver
<table>
<thead>
<tr>
<th></th>
<th>Silver-palladium static-based system a</th>
<th>Silver-palladium dynamic-based system a</th>
<th>Birox 1000 series a</th>
<th>Ruthenium oxide-based system b</th>
<th>Thallium oxide-based system c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sheet resistivity range, Ω/sq.</td>
<td>10 to 10^5</td>
<td>100 to 4 × 10^4</td>
<td>10 to 10^6</td>
<td>10 to 10^7</td>
<td>100 to 10^6</td>
</tr>
<tr>
<td>TCR, ppm/°C, −25° to 125° C.</td>
<td>&lt;300</td>
<td>250</td>
<td>&lt;100</td>
<td>&lt;100 to 500</td>
<td>+50 to −400</td>
</tr>
<tr>
<td>Noise, dBA:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>At 100 Ω/sq.</td>
<td>−18</td>
<td>−18</td>
<td>−30</td>
<td>−35</td>
<td>−30</td>
</tr>
<tr>
<td>At 100 kΩ/sq.</td>
<td>+22</td>
<td></td>
<td>0</td>
<td>+15</td>
<td>−2</td>
</tr>
<tr>
<td>Stability, percent SR:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1000 hr at 30W/in².</td>
<td>&lt;1%</td>
<td>&lt;1%</td>
<td>&lt;0.2%</td>
<td>±0.5% e</td>
<td>0 to 1% d</td>
</tr>
<tr>
<td>1000 hr at 150° C, no load.</td>
<td>&lt;1%</td>
<td>&lt;1%</td>
<td>&lt;0.2%</td>
<td>±0.5% e</td>
<td>0.5% f</td>
</tr>
<tr>
<td>VCR, ppm/V/in. at 10 kΩ/sq.</td>
<td>&lt;−50</td>
<td>−50</td>
<td>−20</td>
<td>±50 to ±200</td>
<td></td>
</tr>
</tbody>
</table>

*Du Pont brochure A–67526 (5M 9/69).
*Summation from several commercial brochures for pastes which are believed to be based on ruthenium oxide.
*Airco Speer brochure.

*Change in resistivity with temperature cycling, Mil. 202, Method 102. Condition “D” except 150° C.
*1000 hr at 175° C, no load.
*After solder dipping.
terminals, and that it is capable of uniformly close tolerances in production with a minimum of process control. Disadvantages are that it is not as stable environmentally as the precious metal-glass films and is not suitable for eutectic bonding.

Initial work on thallium oxide-glass resistors was reported for ceramic substrates having relatively high thermal expansion coefficients such as forsterite, steatite, or titanates. More recent work (ref. 72) describes a series designed for alumina substrates. A thick-film resistor glaze of precision properties that consists of thallium and ruthenium oxides dispersed in a lead borosilicate glaze has also been reported (ref. 73). These have sheet resistivities of 100 Ω/sq to 1 kΩ/sq, TCR values of ±50 ppm, noise less than 25 dB/decade, and stabilities of much better than 1 percent change in resistivity for a wide range of environmental stress conditions.

Other Systems

Many other resistive glaze systems have been described in the literature. The tungsten/tungsten carbide-glass system (ref. 53) was said to offer low cost, chemical stability in oxidizing and reducing atmospheres, and ease of application to ceramic cores. This system is used primarily for low-cost general-purpose resistors. The tantalum/tantalum nitride-glass (ref. 74) system has been reported to offer a wide range of resistivities, a low TCR, good moisture load performance, and low cost. For both of these systems it is necessary to have an inert or slightly reducing firing atmosphere. These two systems are being used commercially in hundreds of millions of devices made annually.

The indium oxide-glass system (ref. 75) has been reported to have a range of sheet resistivities from 10 Ω/sq to 10 kΩ/sq and TCR's less than 500 ppm/°C. The resistivity of indium oxide may be changed by doping with antimony oxide, and resistivity may also be raised by increasing crystallinity of the final resistor material. Resistive glaze systems based on iridium (ref. 76), iridium oxide (ref. 66), ruthenium (ref. 77), and tin oxide (ref. 78) also have been reported.

Theories of Conduction in Metal-Glass Films

Theoretical analyses of the conduction mechanism for glass-metal thick films have been advanced by Melan and Mones (ref. 54), Brady (ref. 79), and Collins (ref. 80). Melan and Mones suggest p-type semiconducting PdO as controlling the conduction in silver-palladium-glass systems. Brady advances a composite of resistive or conductive elements, arranged in a jack-screw fash-
ion, bonded to one another to give electrical conduction. His model requires the observed resistance to equal the resistance of elemental resistors and the constriction resistance observed at points of contact between them. Collins concludes—

that reliance upon contact resistance between physically discrete particles should result in generally unstable electrical properties, and that useful resistive glazes require the selection of a semimetallic type of material which can be incorporated within the glass matrix as a network of very fine but continuous filaments.

With this model the emphasis is placed on bulk rather than surface properties of the conductive material.

Because of the differing thermal expansion characteristics of conductive particles, glassy matrix and substrate of a thick-film resistor, stresses are present in the resistive film. The influence of the stresses was found to be significant in terms of resistivity and TCR, and its mechanism was discussed in a recent paper (ref. 81).

**Thin-Film Resistors**

A number of types of thin-film resistors have been investigated (refs. 82 and 83). In a majority of these applications the resistors are formed on passive, insulating substrates, such as glass or glazed alumina, although thin-film resistor films are also deposited directly on the surface of monolithic circuits (refs. 84 and 85).

The characteristics most desired for thin-film resistors are (ref. 86) high resistivity; low TCR; and stable properties under environmental conditions, such as high and low temperature, varying atmospheres, etc.

Thin-film resistors can be laid down as metals, metallic alloys, oxides, nitrides, or metal-oxide mixtures (cermets). An apparent advantage of thin-film resistor technology is ability to monitor the resistance of the film as it is being deposited. However, when the vacuum system is opened, the resistance of the film can change drastically. It is also necessary to stabilize the resistors by annealing. As a result, control only to ±3 percent is possible without trimming; the majority of thin films are trimmed. Thick-film metal-glass resistors are reacted at temperatures that are too high to permit monitoring while they are being formed. Thin metal films can have sheet resistivities one or two orders of magnitude greater than the bulk resistivity of the metal. However, sheet resistance control and reproducibility are not easily achieved. High-resistivity tantalum films have been prepared by
sputtering (refs. 87, 88, and 89), and have resistivities of $4 \times 10^{-3}$ to $1 \times 10^{-2}$ $\Omega$-cm. Low-density tantalum films, used as resistors on integrated circuits, have sheet resistances from 500 to 2500 $\Omega$/sq (ref. 90). Properties of tungsten, molybdenum, and chromium resistor films have been reported by Rairden (ref. 91). Thermal oxidation is essential to stabilize the metallic films against long-term increases in resistance values. In general, metallic thin films of high-sheet resistivity have not been reproducible and are not stable at high temperatures.

*Metal-oxide or cermet* thin films, such as evaporated Cr-SiO film resistors (ref. 92), have been studied since 1961, and constitute an important segment of thin-film resistors (ref. 93). The Cr-lead oxide glass films have a TCR of about $-0.3$ percent/°C at 6 kilohms/sq sheet resistivity and such resistors have reportedly been used on a monolithic circuit (ref. 94).

Partially oxidized or nitrided tantalum and nichrome thin-film resistors can also be prepared by reactive sputtering of the metal in an argon-oxygen or argon-nitrogen atmosphere. Mixed metal-oxide films have been prepared by simultaneously dc sputtering a nonreactive metal and a reactive metal in an argon-oxygen atmosphere. Such gold-tantalum oxide films (ref. 95) have been prepared with TCR values less than 0.01 percent/°C at 6 to 8 kilohms/sq sheet resistivity. Recent developments in rf sputtering have greatly increased the range of ceramic-type materials which can be utilized for thin-film resistors. This could result in a significant improvement in stable and reproducible high-resistivity films.

*Silicon-metal* films, such as Si-Cr films prepared by electron-beam evaporation and containing 60–69 wt % of Si, have been reported (ref. 96) to have a TCR of $\pm 50$ ppm/°C. Sputtering has also been used to deposit silicon-metal films (ref. 97), and other systems such as Cr-Ge have been studied. The properties of a number of resistive thin films are given in table XII (refs. 98 and 85).

**NASA CONTRIBUTIONS**

NASA has played a strong contributory role in developing and supporting research in screened thick-film circuitry. The Langley Research Center, for instance, has not only developed its own fabrication facility, but has supported considerable external research by industrial companies and universities to advance the state of the art of screened thick-film resistors. The early history of screened metal-glass-type resistors by Du Pont is closely
### TABLE XII.—Resistive Thin Films

<table>
<thead>
<tr>
<th>Class</th>
<th>Material</th>
<th>Resistivity</th>
<th>TCR, ppm/°C</th>
<th>Deposition method</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ω-cm (bulk)</td>
<td>kΩ/sq (sheet)</td>
<td></td>
</tr>
<tr>
<td>Metals</td>
<td>Rhenium</td>
<td>$1 \times 10^{-4}$ to $5 \times 10^{-4}$</td>
<td>0.3 to 7</td>
<td>0 to 200</td>
</tr>
<tr>
<td></td>
<td>Tantalum</td>
<td>$4 \times 10^{-3}$ to $1 \times 10^{-2}$</td>
<td>0.5 to 2.5</td>
<td>-200 to -350</td>
</tr>
<tr>
<td>Alloys</td>
<td>Ni-Cr</td>
<td>$1 \times 10^{2}$ to $2 \times 10^{3}$</td>
<td>0.025 to 0.35</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Co-Cr</td>
<td></td>
<td>0.02 to 2</td>
<td>±30</td>
</tr>
<tr>
<td>Metal on oxide</td>
<td>Al-SiO₂</td>
<td>1 to 20</td>
<td></td>
<td>-3000</td>
</tr>
<tr>
<td></td>
<td>Cr-Pb-glass</td>
<td>1 to 10</td>
<td></td>
<td>-3000 at 6 k/sqΩ</td>
</tr>
<tr>
<td>Metal oxide</td>
<td>Cr-SiO₂</td>
<td>$3 \times 10^{-3}$</td>
<td>1 to 2</td>
<td>-125 ± 50</td>
</tr>
<tr>
<td></td>
<td>Al-Al₂O₃</td>
<td>$1 \times 10^{-2}$ to 1</td>
<td>0.1 to 1</td>
<td>±150</td>
</tr>
<tr>
<td></td>
<td>Au-Ti₅O₇</td>
<td></td>
<td>0.1 to 100</td>
<td>±250</td>
</tr>
<tr>
<td></td>
<td>Au-SiO₂</td>
<td>$10^{2}$ to $10^{6}$</td>
<td></td>
<td>-500 to -5000</td>
</tr>
<tr>
<td></td>
<td>Cr-SiO₂</td>
<td>$10^{-2}$ to $10^{3}$</td>
<td>0.1 to $10^{4}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>NiCr-SiO₂</td>
<td>$10^{-2}$ to $10^{2}$</td>
<td>0.1 to $10^{4}$</td>
<td></td>
</tr>
<tr>
<td>Silicon-metal</td>
<td>Si-Cr</td>
<td>$10^{-3}$</td>
<td>1 to 10</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>Si-Cr</td>
<td>$10^{-4}$ to $10^{-2}$</td>
<td>1 to 20</td>
<td>300 to -600</td>
</tr>
<tr>
<td></td>
<td>Cr₅Si/TaSi₅/Al₂O₃</td>
<td>$5 \times 10^{-4}$ to $2 \times 10^{-2}$</td>
<td>1 to 10</td>
<td>+50 to -300</td>
</tr>
<tr>
<td>Metal nitride</td>
<td>TaN</td>
<td>$2.5 \times 10^{2}$ to $5 \times 10^{3}$</td>
<td>0.025 to 2.5</td>
<td>+100 to -200</td>
</tr>
</tbody>
</table>
linked with Langley Research Center's own needs. Although Du Pont has been instrumental in developing and making commercially available a whole series of palladium-oxide metal-glass resistors, significant work was done at Langley to explain resistor mechanisms in terms of material interactions. Work also was sponsored to extend the useful resistivity range.

The resistance of metal-glass compositions can be adjusted by varying the proportions of conductive phase and glass phase. In 1963, the first successful screened metal-glass resistor series, the palladium-silver series, was limited to a maximum resistivity of about 20,000 $\Omega$/sq without serious loss of quality. To achieve values above 20-kilohm level, the concentration of metal particles was reduced to such a level that the resulting resistors became erratic, nonreproducible, nonlinear, noisy, and unstable. This behavior was basic to all composition systems at that time, and was attributed to a decrease of particle density to the point where quantum mechanical tunneling between particles became significant. To overcome the high-resistance limitation, a research and development program was sponsored at Speer Carbon Co. (now Airco Speer) by Langley Research Center (ref. 99).

Mixtures of thallium oxide and various glasses were studied along with appropriate adjustments of processing. Thallium oxide of 0.2-$\mu$m average particle size was mixed with Harshaw Q-12 glass frit as well as modifications of this glass. Q-12 is basically a lead borosilicate glass having an average particle size of 1.5 $\mu$m and a softening point of 400$^\circ$C. Glasses of varying thermal expansion and softening point were formed by additions of silica, boron oxide, and zinc oxide. It was concluded that the composition of the glass determined the TCR and stability of the resistors by influencing the thermal expansion of the glaze. Thermal expansion mismatches between glazes and substrates caused cracking of the glaze and a lack of stability. Resistor pastes to 1.31 M$\Omega$/sq were developed with TCR's less than 350 ppm/$^\circ$C and a VCR less than 60 ppm/V. Instabilities under various thermal, electrical, and humidity tests were less than 1 percent in most cases. The pastes were especially compatible with ceramic substrates of higher thermal expansions, such as steatite and titanate, although a formulation was devised for use on alumina that was only slightly inferior to the higher thermal expansion coefficient formulations. The project goals and results are summarized in table XIII.

A program was sponsored by NASA at Microtek Electronics, Inc. (ref. 100), to study the reliability of thick-film capacitors, re-
<table>
<thead>
<tr>
<th>Resistor characteristics</th>
<th>Contract guidelines</th>
<th>Compositions utilizing Harshaw Q-12 glass frit</th>
<th>Modified Harshaw Q-12 glass frit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sheet resistivity range, kΩ/sq</td>
<td>300 to 1000</td>
<td>100 to 1310</td>
<td>60.9 to 823.6</td>
</tr>
<tr>
<td>TCR, ppm/°C</td>
<td>±350 (−55° to 125° C)</td>
<td>−247 to −338</td>
<td>−368 to −375</td>
</tr>
<tr>
<td>Power rating, W/in²</td>
<td>10 at 80° C</td>
<td>&lt;1 percent change/1000 hr</td>
<td>&lt;1.7 percent change/1000 hr</td>
</tr>
<tr>
<td>Reliability</td>
<td>Less than ±10 percent change per 5000 hr at 90 percent relative humidity and 150° F.</td>
<td>&lt;0.5 percent change</td>
<td>&lt;4 percent change</td>
</tr>
<tr>
<td>Reproducibility</td>
<td>Deposition accuracy of ±15 percent from the mean.</td>
<td>Satisfactory</td>
<td>Satisfactory</td>
</tr>
<tr>
<td>Substrate compatibility</td>
<td>The pastes shall be suitable for deposition on glasses and various other electro-ceramics including alumina.</td>
<td>Satisfactory</td>
<td>Satisfactory</td>
</tr>
<tr>
<td>Terminal compatibility</td>
<td>The pastes shall be chemically and physically compatible with &quot;fired-on&quot; precious-metal-based conductive pastes.</td>
<td>Satisfactory</td>
<td>Satisfactory</td>
</tr>
</tbody>
</table>
sistors, and conductors. Program objectives included establishing failure criteria for components, identifying failure mechanisms, and providing and analyzing test information.

In the case of resistors, chemical mechanisms of resistor drift were studied for a commercial silver-palladium-oxygen system and specially prepared materials. Important variables that apply to resistor stability within the scope of the program are

1. Chemical composition of the resistor body
2. Sheet resistivity of the resistor material within specific chemical composition
3. The use of a resistor overglaze, be it cofired or low-temperature refire
4. Trimming method—abrasive or laser
5. Firing profile—belt speed versus peak temperature
6. Power density
7. Effect of form factor

The critical measurements used to establish resistor performance were the resistance value, noise, voltage coefficient of resistivity, temperature coefficient of resistivity, and current surge.

The parameters cited above were changed for each of the seven variables. Initial data were gathered during established periods of the first 5000 hr. Test samples were subjected to six times normal rated voltage or 120 W/in² for 5 sec. The reliability data coupled with careful control of process variables should lead to screening criteria for the manufacture of high-reliability thick-film components.

At Goddard Space Flight Center, the thermal and radiation stability of thin-film cermet-resistive elements were investigated (ref. 101). The resistive elements were a mixture of 80% chromium and 20% silicon monoxide developed under a contract with Texas Instruments (ref. 102). The cermet films had a thermal stability of 1 ppm/°C from −50° to +157° C and a radiation stability of ≤1 percent variance in absolute resistance for fluxes up to $1 \times 10^{15} \text{ e/cm}^2$ at a 1.5-MeV energy level. The cermet resistor fabrication technology was shown to be physically compatible with silicon semiconductor integrated circuitry. The cermet thin-film resistors thus offer a stable, wide-range alternative to the inherent instabilities and relatively narrow range of values of present silicon resistors.
Ceramic and Glass Capacitors

Can you envision a hand-sized transistor radio in which a volume equal to that of the radio was needed for just the capacitors? Without development of new capacitor materials and designs, keeping pace with size reduction in other components, this could have come about. What are the dielectric materials used in capacitors, and how have ceramic dielectrics developed (ref. 103) to meet the needs of microcircuitry?

This chapter is about ceramic and glass capacitor technology. Developments that have reduced size with accompanying improvements in quality, and the transition into film and hybrid technology, are described. NASA's contributions have been primarily in spurring the trend to microelectronics. NASA has also enhanced knowledge and awareness of the important material parameters.

At each stage of size reduction, advancing from miniaturization of discrete parts to microelectronics, capacitors have met the challenge of satisfying scaledown specifications. Significant advances in dielectric materials were required to achieve the dramatic increase in capacitance per unit volume by five orders of magnitude over the last three decades (ref. 104). Not only materials but also configurations and manufacturing processes have contributed, resulting in a number of capacitor types. Now large-scale integrated circuitry threatens discrete and film capacitors, and even the use of the capacitor function (ref. 103). Hybrid microcircuitry, on the other hand, utilizes a wide variety of circuit components and can sustain or advance the use of those components that do the most efficient job.

One measure of the utility of competing capacitor materials is their sales. In 1965 the entire capacitor market totaled $390 million. That year, ceramic and glass capacitors provided 1.8 billion units, or 62 percent of the market, although their dollar volume was only 24 percent of the total. The average value of a ceramic capacitor was about 4 cents, while it was about $1 for a glass capacitor. Competitive capacitors ranged from 17 to 60 cents.
each. By July 1969 the volume was up to $425 million per year and the proportion of ceramic and glass capacitors sold was about the same (ref. 105). The introduction of ceramic multilayer capacitors has been an important factor in retaining markets for discrete components, although junction capacitors in integrated circuits are the fastest growing means to supply capacitance to circuitry.

Ceramic and glass capacitors can be made economically when cost is given highest priority, as in home entertainment and many other commercial applications. Aerospace demands usually include radiation fields, high vibrational intensities and g-forces, wide temperature ranges, and surge voltages. Ceramic capacitors can meet these demands also, with close tolerances and high performance, if cost is made a secondary criterion.

CLASSIFICATION OF CAPACITORS

The function of a capacitor is to store an electrical charge, but capacitors display electrical losses arising from currents through the dielectric or from imperfect charge reversal within the dielectric. The degree of loss within a dielectric (its dissipation factor) is only one of the characteristics of the various types of capacitors. Other important features are capacitance per unit volume, temperature coefficient of capacitance (TCC), degradation under electric field for extended periods of time, capacitances available, voltage dependence, capacitance tolerances, electrical breakdown strength, frequency response, radiation tolerance, ruggedness, stability, configurations available, and cost. It is the overall performance of a capacitor in a given design that determines which type is used. Capacitance ranges of the basic types of capacitors are shown in figure 13, and their advantages and disadvantages are listed in table XIV (ref. 106).

Ceramic and glass capacitors possess very low to intermediate capacitances. Glass capacitors combine low values with enduring stability in extremes of temperature, voltage, and frequency. The lower capacitance range is also satisfied by the temperature compensating type. These capacitors are available in different TCC's, from positive to negative values. Circuitry variations with temperature can be compensated with the right combination of capacitance and TCC. The high-dielectric constant, general-purpose ceramic capacitors offer good volumetric efficiency, flexibility in size and shape, ruggedness, inherent reliability, and low cost; their properties can also be tailored over wide ranges. Their principal disadvantage is a tradeoff of stability for high
Capacitors come in either fixed (nonvariable) or variable types (ref. 107). In many circuits, a change in capacitance is needed. Variable capacitors serve this function. Most of these capacitors change capacitance by varying the electrode area where air is the dielectric medium. Other designs change the electrode area over a solid dielectric to vary capacitance. This chapter is limited to the use of ceramics and glasses in nonvariable capacitors.

**CERAMIC CAPACITORS**

The following section describes types, properties, configurations, and designs which combined give the ceramic capacitor its appeal to the electronic design engineer.

**Temperature Compensating Capacitors**

As the temperature of a circuit rises because of heat given off by resistors, inductors, and active circuit elements, the properties of all components will change to some measurable degree. The temperature change in properties is inherent in many circuit components, very difficult to eliminate in others, or unavoidable due to cost considerations. However, accurate compensation for the changes with temperature can be made in critical circuits by
Table XIV.—Advantages and Disadvantages of the Major Types of Capacitors

<table>
<thead>
<tr>
<th>Capacitor type</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Applications and comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ceramic:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a) Low K a glass and ceramics.</td>
<td>Excellent stability with time, temperature, voltage, and frequency.</td>
<td>Low K, low capacitances available.</td>
<td>Stability and reliability dictate use.</td>
</tr>
<tr>
<td>(b) Temperature compensating...</td>
<td>Linear, variable TCC, low cost, and high stability.</td>
<td>Low volumetric efficiency.</td>
<td>Temperature compensating; used to correct circuit changes with temperature, low capacitance needs.</td>
</tr>
<tr>
<td>(c) High K or general purpose...</td>
<td>Good volumetric efficiency, tailoring of properties to meet the need, low cost.</td>
<td>High K is achieved at the expense of stability.</td>
<td>General-purpose usage and hybrid microcircuitry.</td>
</tr>
<tr>
<td>(d) Semiconducting...</td>
<td>High capacitance at low cost in a small volume.</td>
<td>Low voltage use, low insulation resistance, very voltage dependent, and low reliability when operated at rated voltages.</td>
<td>Conventional circuitry: high capacitance in a small size, characteristics similar to electrolytics, has a dielectric film on a semiconducting substrate.</td>
</tr>
<tr>
<td>(e) Monolithic, available in materials (a), (b), and (c) shown above.</td>
<td>Good volumetric efficiency, wide range of capacitances in small volumes.</td>
<td>Stability is limited in the high-K materials.</td>
<td>Microcircuitry: chip capacitors to deliver high capacitance in small volumes; usable in film circuits.</td>
</tr>
<tr>
<td>Mica...</td>
<td>Low cost and low losses.</td>
<td>Low volumetric efficiency.</td>
<td>Frequency determination is the main application. Competitor is stable ceramics. Only natural mineral used as a capacitor dielectric.</td>
</tr>
<tr>
<td>Capacitor Type</td>
<td>Characteristics</td>
<td>Notes</td>
<td></td>
</tr>
<tr>
<td>---------------</td>
<td>-----------------</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td>Air and vacuum</td>
<td>Low losses and extreme stability.</td>
<td>Low $K$, vacuum must be contained in a glass tube.</td>
<td></td>
</tr>
<tr>
<td>Paper</td>
<td>Low cost.</td>
<td>Tuners: air-variable capacitors are the only units that use air as a dielectric, used to tune radios. Tank tuning: for high frequency; high power units are made of vacuum variable capacitors.</td>
<td></td>
</tr>
<tr>
<td>Plastic film</td>
<td>Better electrical properties and smaller size than paper capacitors. Low dielectric absorption. A variety of films, each having a special advantage, is available.</td>
<td>Coupling: takes low-frequency current well.</td>
<td></td>
</tr>
<tr>
<td>Electrolytic</td>
<td>High volumetric efficiency.</td>
<td>Coupling and bypass: up to 1 MHz for Mylar® and 1 GHz for Teflon®, polystyrene and polycarbonate.</td>
<td></td>
</tr>
<tr>
<td>(a) Aluminum</td>
<td>Low cost.</td>
<td>Bypass and filtering: excess rf current must not flow through capacitor; ac component must be less than dc working voltage.</td>
<td></td>
</tr>
<tr>
<td>(b) Tantalum</td>
<td>Has an oxide film (TaO₅) of higher $K$ than that of aluminum type (Al₂O₃). Tantalum-electrolyte system is very stable.</td>
<td>Polarity. Need 2 polar capacitors back-to-back to form a nonpolar unit.</td>
<td></td>
</tr>
</tbody>
</table>

* Relative dielectric constant.

® Registered trademark of E. I. du Pont de Nemours & Co., Inc.
utilizing ceramic temperature compensating capacitors (NP0 type). These capacitors can be made with temperature coefficients of capacitance of +120 through 0 to −5600 ppm/°C. Dielectric constants of 15 to 95 are available, as are extreme stability, control of the TCC, and low losses (ref. 108).

The use of ceramic materials formulated especially for capacitor applications began with the discovery of the high dielectric constant of titanium dioxide (~100). By adding magnesia to titania and controlling the proportions, it was learned that the TCC could be varied. The compositional series, magnesia-titania and barium titanate-titania, constitute two examples of the NP0 series of compositions made commercially. Additions to barium titanate of SnO$_2$, Nb$_2$O$_5$, Ta$_2$O$_5$, and bismuth stannate have been used for lowering TCC and flattening the peak in capacitance around the Curie temperature. Grain refinement has also been used to improve stability of capacitance to temperature variations. Most of the published work on control by additives is based on solid solutions of the added cation in the barium titanate phase. It is also possible to modify the TCC by controlled additions of appropriate secondary phases. Figure 14 illustrates the range of dielectric constants obtainable with varying values of TC for several series of compositions of the NP0 series (ref. 109).

**High Dielectric Constant Capacitors**

As the electronic industry has sought greater capacitance in smaller sized units, the ceramic capacitor industry has satisfied the demand. In the 1930's the capacitance in a unit of about 1/2 by 1/2 by 3/16 in. was 100 pF. In the early 1940's the advent of barium titanate brought this value to 1000 pF. Modifications in the formulation of barium titanate increased the value to $10^4$ pF. By the mid-1950's transistors came into common usage, and lower voltages were possible. The reduction of the dielectric thickness and improved formulations produced a capacitor of $10^5$ pF. The development of the reduced titanate capacitor in the late 1950's afforded a capacity of $10^6$ pF or 1 μF; however, the thickness of the dielectric limited voltages to 3 to 6 V. Finally, by 1968, techniques were perfected to produce multiple stacks of dielectrics and electrodes culminating in a 10-μF capacitor. This stacked array has 50 to 80 layers of a material with a nominal $K$ value of 6000 to 7000, about 0.002 in. thick (refs. 104 and 110), and is no larger in overall dimensions than the 1930 capacitors.

---

"Designates negative, positive, and zero (0) temperature coefficients of capacitance."
Figure 14.—Dielectric constant versus TCC for temperature-compensating ceramic dielectric materials.

Figure 15 indicates $K$ versus temperature for types of high- and intermediate-$K$ materials in general use (ref. 109). (The curves for $K$–2000 and $K$–8000 were suggested by D. W. Hamer.) Table XV shows a compilation of pertinent capacitor properties for selected capacitor compositions of this class of materials. In general, stability, voltage, and temperature dependence, and dielectric strength deteriorate as the dielectric constant is increased. Also degradation under sustained dc fields is increased. The reason for this behavior can be traced to the mechanism of the electrical storage in high-$K$ materials.

High-$K$ ceramics offer wide choices in $K$, Curie temperature, and constancy of $K$ with ambient temperature variations because of knowledge derived from extensive research on control of properties through control of chemical composition and microstructure. The barium titanate (BaTiO$_3$) lattice is very adaptable to isomorphous substitutions for Ba, Ti, or O (refs. 111 to 113). Elements which do not go into substitution positions can be located in secondary crystalline or glassy phases which may further affect properties by their relative thermal expansions, bonding, proportions, and distributions. This wide range in compositional variation and flexibility in properties is available only in the polycrystalline ceramics and cannot be matched in single crystals.
The $K$ of barium titanate ceramics may also be varied by controlling grain size. This is illustrated in figure 16 (ref. 114). It can be seen that the $K$ increases as the grain size decreases to 1 μm. The subsequent decrease in $K$ for grain sizes smaller than 1 μm has been refuted by some investigators. The reason for this behavior is not fully understood although there have been continual improvements in the basic understanding of the high-$K$, fine-grained ceramics based on thermodynamic theory and internal stress models.

**Semiconducting Ceramic Capacitors**

Barium titanate ceramics are capable of being reduced to a semiconducting state and also of being reoxidized. By reducing a slab of barium titanate completely, and then reoxidizing only its surface, it is possible to form a thin layer of high dielectric constant materials (ref. 116). One construction of this kind of capacitor, the reoxidized layer type, is shown in figure 17 along with the following diagram:

![Diagram showing dielectric constant versus temperature curves for intermediate and high dielectric constant titanate dielectrics.](image)
Table XV.—Typical Property Data for High Dielectric Constant Ceramic Materials

[Ref. 108]

<table>
<thead>
<tr>
<th>Material designation</th>
<th>K-0270</th>
<th>K-120C</th>
<th>K-2000</th>
<th>K-6000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Median dielectric constant</td>
<td>280</td>
<td>1275</td>
<td>2150</td>
<td>6300</td>
</tr>
<tr>
<td>Insulation resistance, ( \Omega \cdot \text{cm} \times 10^{10} )</td>
<td>4.0</td>
<td>10.0</td>
<td>4.0</td>
<td>1.25</td>
</tr>
<tr>
<td>Aging, percent per decade</td>
<td>2.0</td>
<td>.5</td>
<td>3.5</td>
<td>4.0</td>
</tr>
<tr>
<td>Voltage coefficient of capacitance, percent, at:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 V dc per mil</td>
<td>( \pm 1 )</td>
<td>( \pm 1.0 )</td>
<td>( \pm 2.0 )</td>
<td>(-25.0)</td>
</tr>
<tr>
<td>20 V dc per mil</td>
<td>( \pm 1 )</td>
<td>( \pm 3.0 )</td>
<td>(-4.0)</td>
<td>(-55.0)</td>
</tr>
<tr>
<td>30 V dc per mil</td>
<td>( \pm 5.0 )</td>
<td></td>
<td>(-12.0)</td>
<td>(-80.0)</td>
</tr>
<tr>
<td>50 V dc per mil</td>
<td>(-12.0)</td>
<td></td>
<td>(-17.0)</td>
<td>(-85.0)</td>
</tr>
<tr>
<td>Dielectric strength, V/mil, at:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.010-in. thickness</td>
<td>300</td>
<td>350</td>
<td>200</td>
<td>135</td>
</tr>
<tr>
<td>0.020-in. thickness</td>
<td>300</td>
<td>300</td>
<td>180</td>
<td>135</td>
</tr>
<tr>
<td>0.030-in. thickness</td>
<td></td>
<td>250</td>
<td></td>
<td>135</td>
</tr>
<tr>
<td>0.040-in. thickness</td>
<td></td>
<td></td>
<td>200</td>
<td>135</td>
</tr>
<tr>
<td>0.050-in. thickness</td>
<td></td>
<td></td>
<td>175</td>
<td>110</td>
</tr>
<tr>
<td>Frequency variation of dielectric properties, percent, at:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 kHz:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Base capacitance</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Power factor</td>
<td>.3</td>
<td>1.3</td>
<td>1.3</td>
<td>1.3</td>
</tr>
<tr>
<td>10 kHz:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Capacitance change, ( \Delta C )</td>
<td>(-2.0)</td>
<td>(-.6)</td>
<td>(-1.0)</td>
<td>(-3.0)</td>
</tr>
<tr>
<td>Power factor, ( \Delta PF )</td>
<td>.4</td>
<td>1.7</td>
<td>1.35</td>
<td>1.2</td>
</tr>
<tr>
<td>100 kHz:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \Delta C )</td>
<td>(-2.0)</td>
<td>(-2.0)</td>
<td>(-3.5)</td>
<td>(-6.0)</td>
</tr>
<tr>
<td>( \Delta PF )</td>
<td>.4</td>
<td>2.7</td>
<td>1.4</td>
<td>1.0</td>
</tr>
<tr>
<td>1 MHz:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \Delta C )</td>
<td>(-10.0)</td>
<td>(-5.0)</td>
<td>(-4.0)</td>
<td>(-7.0)</td>
</tr>
<tr>
<td>( \Delta PF )</td>
<td>.5</td>
<td>5.2</td>
<td>1.5</td>
<td>.9</td>
</tr>
<tr>
<td>10 MHz:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \Delta C )</td>
<td>(-12.0)</td>
<td>(-19.0)</td>
<td></td>
<td>(-8.0)</td>
</tr>
<tr>
<td>( \Delta PF )</td>
<td>.8</td>
<td>9.2</td>
<td></td>
<td>.9</td>
</tr>
</tbody>
</table>

with its equivalent circuit. The working voltage of this capacitor is 18 to 30 V. A second type, called the “barrier layer,” can be formed by treating the reduced disk so that the surfaces of grains throughout the disk are reoxidized. This capacitor is limited to about 12 V, and its properties are very voltage and frequency dependent, but it offers high capacitance in a small volume (ref. 117).
Configurations and Designs

A major reason for the acceptance of ceramic capacitors has been their great flexibility in configurations and designs (ref. 118). Most capacitors are of simple shape (tubes, disks, or plates), and leads are either attached wires or silver-glass areas fired onto the surface of the capacitor. These simple shapes are also used in feedthrough or standoff designs when the mounting is used to perform a mechanical or special electrical function. However, there are a great many ways to form and shape ceramics while retaining or enhancing their desirable properties. This flexibility in shaping is used in high-value capacitors for microcircuitry (ref. 119). Figure 18 shows a number of configurations using a "monolithic multilayer" construction in which several thin layers are placed on top of each other to build up total capacitance. Figure 18(a) shows a typical construction while 18(b), (c), (d), and (e) show unusual configurations (ref. 118).

The use of small, discrete, unencapsulated (or "chip") capacitors is a popular way of achieving capacitance in microcircuitry. Much of the demand is being met by multilayer ceramic capacitors, although tantalum capacitors can provide values of 1 μF and higher. For this application, the K-1200 formulation offers
The best compromise between electrical performance and size requirements (ref. 120). The multilayer construction is also useful for high-voltage applications. In conventional construction of capacitors, electrode-ceramic-encapsulation interfaces are troublesome. Arc-over along the surface is decreased by lengthening the surface distance between electrodes, being careful about cleanliness, and avoiding poor interface adhesion. By using multilayer construction for high voltages, the electrodes are encapsulated in the dielectric itself. There is no opportunity for contamination and no exposed surface for arc-over. The edges of the electrodes are surrounded by a uniform dielectric-constant material, which reduces electric field intensity peaks. Finally, the electrodes are of noble metal and are not degradable in high fields, as glass-metal systems might be in conventional capacitors. Examples of single dielectric layer designs to minimize arc-over are shown in figure 19.

The multilayer construction can also be used with other ceramic materials; e.g., NP0 compositions or alumina. Alumina has been used as the dielectric for transmitter capacitors. Transmitter capacitors handle high-radiofrequency voltages and currents, and a low dissipation factor is required to minimize losses. A common solution employs vacuum capacitors. However, such capacitors require large volume and are expensive. Alumina has
USE OF CERAMICS IN MICROELECTRONICS

Buried Electrodes
Ceramic
Fired On "Collector"
Electrodes
(a)
(b)
(c)
(d)
(e)

**FIGURE 18.**—Construction features of various multilayer ceramic configurations. (a) Typical multilayer construction (rectangular planar configuration). (b) Discoidal configuration. (c) Tubular configuration. (d) Single buried layer (for trimmer rotor). (e) Curved bank configuration.

high dielectric strength and low losses; also, high operating temperatures do not degrade its performance. These factors provide good volumetric efficiency (ref. 118).

**GLASS AND GLASS-CERAMIC CAPACITORS**

Glass capacitors are known for the reliability resulting from their uniformity, simplicity, inherently stable properties, and highly predictable behavior. Originally, glass capacitors were based on thin sheets of a lead borosilicate glass and aluminum foil. Since the advent of glass ceramics, capacitor designs have appeared in which advantage is taken of the higher dielectric constants and lower losses attainable by deliberately crystallizing high-K phases from a previously amorphous glass (refs. 121 to 124). The electrical properties available are determined by the individual properties of crystalline and glass phases, their relative amounts, their interaction, and the nature of the microstructure.
Figure 19.—Three low corona designs for high voltage ceramic capacitors.

Figure 20.—Cross-sectional micrograph of the monolithic multilayer construction of a glass-ceramic capacitor.

Figure 20 shows the pore-free structure of a recently developed, multilayer, glass-ceramic dielectric. Recent advances have demonstrated that high-\(K\) ceramics can be sintered to a pore-free microstructure, although the process is time consuming and expensive. The photograph shows that glass dielectrics can be
made very homogeneous and relatively free of internal micro-
flaws. Construction is also simple since the glass or glass ce-
ramics used for the dielectric can form not only the capacitor but
also its packaging system. The benefits are the same as those of
monolithic multilayer ceramic capacitors—electrodes and elec-
trode attachments are completely embedded in a hermetically
sealed, uniform dielectric. Shortcomings are that for a given
value of TCC*, the glass-ceramic capacitors have a lower K and
also a lower energy storage capability.

Glass is a very stable material. Figure 5 (in ch. 2) shows di-
electric breakdown, loss tangent at 1 Mc, and dc resistivity as
functions of temperature for several commercially available
glasses. The capacitor glass cited has been optimized for elec-
trical properties while its good forming properties have been re-
tained. These data illustrate that the electrical properties of
glass are retained at the temperatures involved in most circuitry.
The properties also change more uniformly than do those of crys-
talline dielectrics. Unless electrolysis occurs, with subsequent
heterogeneities, the change in properties with temperature is
reversible.

One type of glass capacitor is available in a 1- to 2400-pF range
of capacitance. For a thickness of 0.15 in., the size varies from a
length of 0.3 in. and a width of 0.2 in. to a length of 0.5 in. and a
width of 0.3 in. The temperature coefficient is 140±25 ppm/°C
and losses are less than 0.1 percent for capacitance greater than
100 pF and less than 0.2 percent for values below 100 pF. The
change in capacitance after 2000 hr at 125° C at 150 percent of
rated voltage is less than 0.5 percent. The performance charac-
teristics of commercially available multilayer chip capacitors of
glass ceramics are shown in table XVI (ref. 125). A wider range
of capacitance is available in this class of glass ceramics that uti-
lizes a ferroelectric crystalline phase. However, this advantage
is achieved at the expense of stability.

**SUBSTRATE AND FILM CAPACITORS**

In hybrid circuits, capacitance can be derived by using the sub-
strate as a capacitor dielectric or by film techniques as alterna-
tives to discrete capacitors.

**Substrate Capacitors**

Capacitative elements of microcircuits are sometimes formed
by using the substrate itself as the dielectric medium. Metallic
areas on either side of the substrate form electrodes, and these
TABLE XVI.—Characteristics of Commercial Tubular Glass-Ceramic Capacitors

<table>
<thead>
<tr>
<th>Capacitance range, pF</th>
<th>Maximum length, in.</th>
<th>Maximum diameter, in.</th>
<th>Temperature coefficient, percent</th>
<th>Dissipation factor, percent</th>
<th>Variation in lifetime capacitance, percent (maximum)</th>
</tr>
</thead>
<tbody>
<tr>
<td>270 to 10,000</td>
<td>0.250</td>
<td>0.100</td>
<td>+2, -10</td>
<td>1.0</td>
<td>2.0</td>
</tr>
<tr>
<td>12,000 to 20,000</td>
<td>0.250</td>
<td>0.100</td>
<td>+2, -15</td>
<td>1.5</td>
<td>5.0</td>
</tr>
<tr>
<td>22,000 to 39,000</td>
<td>0.250</td>
<td>0.100</td>
<td>+20, -45</td>
<td>3.0</td>
<td>20.0</td>
</tr>
<tr>
<td>47,000 to 51,000</td>
<td>0.250</td>
<td>0.100</td>
<td>+20, -45</td>
<td>3.0</td>
<td>20.0</td>
</tr>
<tr>
<td>56,000 to 100,000</td>
<td>0.250</td>
<td>0.140</td>
<td>+20, -45</td>
<td>3.0</td>
<td>20.0</td>
</tr>
</tbody>
</table>
are interconnected into the circuit. Multiple ceramic capacitors on a single substrate with wire leads have been available for about 20 yr, and the use of the insulating dielectric as the mounting for other components seems logical. Where the capacitance requirements are low, the common substrates such as alumina can be used. If high values of capacitance are needed, high dielectric constant substrates of titanate composition may be used. However, these offer at least two disadvantages: poor thermal shock properties due to the high thermal expansion coefficient and low strength of barium titanate, and large values of stray capacitance between conductors. There is also a lack of circuit versatility in attempting to use substrates in dual functions.

**Thick-Film Capacitors**

Thick-film capacitors are classified into high-$K$ or high-$Q$ groups ($Q$ is the ratio of energy stored to the amount dissipated per cycle). Each is further complicated by the choice of electrode compositions. High-$K$ capacitors (refs. 126 to 130) achieve high capacitance in a small area by blending high-$K$ ferroelectric materials with various other dielectrics, modifiers, and vehicles, forming a thick-film pattern, and firing to maturity. Addition of lower $K$ materials controls capacitor properties such as temperature and voltage coefficients of capacitance.

Thick-film capacitors are usually applied by silk screening the dielectric-containing pastes onto a substrate. A low-melting glass is included in the paste formulation for bonding the dielectric particles into a desirable microstructure, as well as for joining the resultant ceramic film to the substrate.

Effective $K$'s range from 300 to about 1000 with the high-$K$ formulas. Lower $K$'s down to less than 10 are obtained with glasses alone. Intermediate values are obtained by mixtures of high- and low-$K$ materials. For example, addition of only 1 percent of a glass will reduce the high $K$ of the titanate (1000 to 2000) to about 350.

In comparison to discrete titanate capacitors, the highest $K$ realized in thick films is low; but in comparison to single-phase glass capacitors, it is high. The actual capacitance obtained with thick-film compositions is a function of processing conditions, such as thermal history, as well as the type of electrode. Usually an increase in firing temperature over a range from 760° to 1050° C results in an increase of capacitance. At a firing temperature of 950° C, a typical capacitance density translates to about 80 000 pF/sq in. with a dissipation factor below 2 percent.
The temperature coefficient is \(-15\) percent between \(25^\circ\) and \(-55^\circ\) C and is relatively flat \((-7\) percent) between \(25\) and \(85^\circ\) C. Because such high-capacitance formulas have higher losses at high frequencies \((Q=25\) at \(70\times10^6\) Hz\), they are used as blocking or bypass capacitors (ref. 131).

For radiofrequency and intermediate-frequency circuitry, where capacitance density is not a major concern, as are temperature stability and \(Q\), thick films of crystallizable glasses are applicable (refs. 131 to 133). One commercially available composition (ref. 132) has a dielectric constant of \(10\) to \(15\), a dissipation factor of less than \(1.5\) percent and a \(Q\) of \(500\) to \(700\). TCC is linear at about \(1\) percent from \(25^\circ\) to \(125^\circ\) C. A capacitance density of \(1800\) pF/sq in. is possible with this body. High-\(Q\) capacitors have also been developed based on titanium dioxide with capacitances of \(19\) 500 pF/sq in. and high \(Q\) to \(5\times10^8\) Hz. They have been found useful for tuning applications.

In summary, screen-printed, thick-film capacitors afford much promise and merit continued development. They are compatible with the components of thick-film circuitry that they contact (substrates, electrodes), and have been developed to match the printing and firing characteristics of present conductor and resistor compositions. Compared to discrete ceramics, they show low levels of ferroelectric behavior, and their performance is stable at relatively high frequencies. Disadvantages include low capacitance per unit area, poor reproducibility and the constraints on minimum film thickness imposed by load-life requirements. For their high capacitance values, they are presently more expensive than discrete capacitors. Their acceptability may be improved if research in progress leads to higher \(K\) materials and processes with higher yields and assured reproducibility.

**Thin-Film Capacitors**

Thin-film capacitors are usually parallel plates in three layers: conductor/insulator/conductor. In thin-film circuitry, the criteria for designing a capacitor include sufficiently high capacitance, insulation, and breakdown strength. Two major variables that influence the characteristics of thin-film capacitors are the properties of the dielectric material and the film thickness. The materials commonly used have a dielectric constant between \(2\) and \(10\), although anodized tantalum has a \(K\) of \(30\) to \(50\). Other materials, such as the titanates, with a higher \(K\) are available but have not yet been used commercially. Therefore, the thickness of the dielectric becomes an important variable in thin-film capacitor
technology and is closely related to the methods of preparation. In addition, thin-film capacitors must meet other requirements, such as microdimensional characteristics, high initial reliability, and ability to withstand harsh environments, such as are encountered in space.

The commonly used ceramic thin-film dielectrics, their methods of preparation, and properties are summarized in table XVII. "Silicon monoxide" deposited in vacuum has been used extensively. The material is highly sensitive to deposition parameters, with the dielectric constant varying by 25 percent and having a maximum value of about 6. Silicon dioxide and aluminum oxide films have been formed by reactive sputtering (ref. 134). Starting from silicon monoxide and aluminum, and evaporating in high partial pressures of oxygen, films of either oxide alone, or their combinations, have been deposited to provide a wide range of dielectric properties from which desired values could be selected. Tantalum oxide has probably been the most highly investigated thin-film dielectric. It is most often formed by anodic oxidation of evaporated tantalum metal films, although reactive sputtering of the oxide also is employed.

In addition to the material and design requirements, processing control for reproducibility and reliability has posed difficult problems. This has been true particularly for film capacitors with a capacity of more than a few hundred picofarads and voltage ratings above 10 to 30 V. One inherent reason for the difficulty of fabricating thin-film capacitors is that one minute flaw anywhere in the dielectric can lead to catastrophic breakdown of the entire unit. To minimize this danger, dielectric layers are applied to substrates of thicknesses several times greater than indicated by the intrinsic properties of the material.

In addition to the materials listed in table XVII, work has been done on preparing thin films of other inorganic materials such as BaTiO₃ and PbTiO₃ (ref. 135). However, stoichiometry control

<table>
<thead>
<tr>
<th>Material</th>
<th>Preparation technique</th>
<th>Dielectric constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>&quot;SiO&quot;</td>
<td>Thermal evaporation</td>
<td>4.4–6.3</td>
</tr>
<tr>
<td>SiO₂</td>
<td>Thermal oxidation</td>
<td>3.78</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>Anodization-reactive sputtering</td>
<td>10</td>
</tr>
<tr>
<td>Ta₂O₅</td>
<td>Anodization-reactive sputtering</td>
<td>30–50</td>
</tr>
<tr>
<td>Si₃N₄</td>
<td>Pyrolytic decomposition</td>
<td>12.7–13.5</td>
</tr>
</tbody>
</table>
problems have not been resolved, and thin-film capacitors based on these high-K materials are not commercially available. Current efforts using techniques such as rf sputtering offer considerable promise for forming good thin films of high-K ferroelectrics.

Organic films have also been considered, because in spite of their low dielectric constants (2 to 4), films only a few hundred angstroms thick have been made free of flaws. These have been achieved by the polymerization of gaseous monomers with ultraviolet radiation or electron bombardment.

**Tantalum Integrated Capacitors.**

Tantalum is presently the most versatile thin-film material for passive, integrated-circuit components, including capacitors (ref. 136). Tantalum capacitor and resistor preparation includes sputtering (reactive and cosputtering) tantalum thin films, followed by anodization. Tantalum thin-film capacitors have a greater capacitance per unit area than other types of thin-film capacitors. This is because of the high dielectric constant ($K=22$) and high dielectric strength ($6.5 \times 10^6$ V/cm) of anodically grown tantalum oxide films.

The simple tantalum (TM) capacitor consists of an oxide film between a tantalum electrode and an evaporated gold or aluminum counterelectrode. The dielectric strength of these capacitors is high, but they are moisture sensitive. Moisture sensitivity is greatly reduced in a second type of design by using a counterelectrode of nichrome or titanium followed by gold or aluminum. This "adherent counterelectrode"-type capacitor meets stringent stability requirements and is used on Bell Telephone's Touch-Tone® tone-generating circuitry. A third type of tantalum metal capacitor, called the "aluminum underlay" capacitor, is used in high-frequency circuits.

The tantalum metal, manganese-dioxide (TMM) capacitor is a modification of the tantalum metal type and contains a layer of semiconducting manganese dioxide over the Ta$_2$O$_5$ (ref. 136). The manganese dioxide, which is an oxygen-deficient semiconductor, provides a healing effect for weak spots or incipient failures in the Ta$_2$O$_5$ film. Therefore, higher stresses and thinner films can be employed in this type of capacitor, yielding values of up to 5 $\mu$F—about 10 to 100 times greater than the capacitance of the tantalum metal-type capacitors. Also, unlike the TM type, the TMM capacitors can be deposited onto unglazed, rough-surfaced ceramic substrates. The TMM capacitor has superior

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capacitance density and maximum working voltage to the TM type, but it has a higher dissipation factor and TCC.

In another modification of tantalum-based capacitors, a layer of silicon monoxide is evaporated between the Ta$_2$O$_5$ and the counterelectrode. This is a very-low-value capacitor; its capacitance depends on the thickness of the silicon monoxide layer. The Ta$_2$O$_5$ provides the dielectric strength and increases the yield. Figure 21 shows types of tantalum-based capacitors (ref. 136).

**NASA CONTRIBUTIONS**

NASA contributions to capacitor development resulted from space-mission needs for reduced size and weight and increased reliability. When the microelectronic program began at NASA Langley Research Center (LaRC), sufficiently small and reliable capacitors were not available in discrete, film, or integrated chip form, and it was necessary to pioneer the development of capacitors for thick films.

Stermer and McIntosh at NASA LaRC originated work on screened capacitors around 1962. Later D. R. Ulrich joined the Microelectronics Group at NASA LaRC and introduced new concepts in compositions and techniques for thick-film capacitors. This group under the leadership of C. M. Husson also pioneered in concepts of multilayer capacitors and sponsored work on multilayered capacitors at Rutgers, the State University School of Ceramics, with D. A. Lupfer as project leader.

The initial work at NASA LaRC, under Stermer, was inspired by thick-film techniques studied at such places as Gulton Industries. The concept was to screen-print thick films of a mixture of barium titanate, glass powders, and organic vehicles onto an appropriate ceramic substrate. Alumina was early selected as the substrate because of Du Pont's development of Ag-Pd resistors in a glass matrix that matched the TCE of alumina and because of the desirable properties of alumina ceramics.

It was soon realized that the capacitor was the least reproducible and reliable of all electronic components in thick-film microcircuitry. Although the $K$ of the composite approached 100, further research sought even higher values.

As a graduate student under E. J. Smoke at Rutgers, the State University, Ulrich had studied the deposition of undiluted barium titanate by flame spraying. This work had been a part of the long-term Rutgers project, under U.S. Army Electronic Command sponsorship, on ceramic materials for electronics (ref. 137). It was discovered that the rapid quenching inherent in hot spraying
FIGURE 21.—Tantalum-based capacitors. (a) The simplest kind of tantalum thin-film capacitor is comprised of a tantalum pentoxide dielectric sandwiched between a tantalum electrode and a gold counterelectrode. (b) Better yield and electrical performance are exhibited by a TMM (tantalum-manganese-metal) capacitor. (c) This type of capacitor has a low effective dielectric constant and is used for low value capacitors.
permitted barium titanate to be cooled as a glass. Subsequently, heat treatment developed a controlled crystallization to the ferroelectric, high-$K$, perovskite structure.

By 1963, NASA Langley Research Center was working on concepts of materials and techniques for producing multilayered film capacitors and other circuit elements. A project was sponsored at Rutgers, the State University, to reduce the thickness of electronic ceramics (ref. 138). This study established shrinkage and porosity properties of selected ceramics and the variation of $K$ with temperature and frequency. It was determined that layers could be made as thin as 0.0015 in. in multilayered construction and as thin as 0.004 in. in single-layered pieces. Temperature-compensating formulations displayed the most stable properties with temperature and frequency. A bismuth-containing composition ($K$–1200) showed excessive loss at higher frequencies and was not recommended. A $K$–6000 composition worked very well and was believed better than bulk material. Stermer (ref. 139) reported dielectric constants approaching 100 for films of ceramic dielectric particles suspended in a glass matrix. Ulrich furthered thick-film dielectrics for capacitors by preparing composite films (refs. 140 and 141). Previously, low-$K$ thick films consisted of ceramic, high-dielectric-constant particles suspended in a lead borosilicate glass. Because of the low volume of dielectric particles (35 wt %), the $K$'s of the films were less than 100. The suspension also resulted in low-density structures showing high dissipation factors. Ulrich developed techniques to obtain high-$K$ films ($K$ of 300 to 800) by suspending barium titanate particles in a barium titanate-base glass and then crystallizing the glass. The final dielectric consisted of the original suspended barium titanate particles, a precipitated barium titanate crystalline phase, and a residual glass phase. This technique resulted in films containing 90 to 95 percent of barium titanate crystals and suitable for deposition onto alumina substrates. As an example, the compositions of two dielectric films are shown in table XVIII, and the composition of the barium titanate glass is shown in table XIX.

<table>
<thead>
<tr>
<th>TABLE XVIII.—Composition of Dielectric Films</th>
</tr>
</thead>
<tbody>
<tr>
<td>Component</td>
</tr>
<tr>
<td>Barium titanate glass</td>
</tr>
<tr>
<td>Barium titanate microcrystals</td>
</tr>
</tbody>
</table>
Table XIX.—Composition of Barium Titanate Glass

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Amount, wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaO</td>
<td>54.7</td>
</tr>
<tr>
<td>BaF₂</td>
<td>3.2</td>
</tr>
<tr>
<td>TiO₂</td>
<td>24.0</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>7.9</td>
</tr>
<tr>
<td>GeO₂</td>
<td>2.0</td>
</tr>
<tr>
<td>SiO₂</td>
<td>8.2</td>
</tr>
</tbody>
</table>

At room temperature and 10 kHz, the dielectric constants of the two materials, A and B, were respectively: 615±25 and 325±10. These represent capacitance densities of 77 400 pF/in² and 24 800 pF/in². The TCC's were positive to 140° C, the Curie temperature of the composite films. Ulrich also studied the devitrification properties of BaO-TiO₂-SiO₂ and BaO-TiO₂-GeO₂ compositions that contained one, two, or three additional components. Using differential thermal analysis and X-ray techniques, he defined the boundary conditions for devitrification; he also determined each composition's electrical properties as functions of temperature and frequency.

Langley Research Center's Microelectronics Group also sponsored a 3-yr program at IIT Research Institute, with A. J. Mountvala as principal investigator (ref. 142), in which the major emphasis was on the electronic characterization of surfaces and grain boundaries in BaTiO₃ particulates and sintered ceramics. Research effort was directed toward the following factors:

1. The properties of the surface layer of powder particulates, and how they change with particle size, processing history, and environmental partial pressure.

2. The electrical properties of the boundary phase in polycrystalline materials and their relationship to grain size and disorientation.

3. Possible correlation between the characteristics of the surface layer of the powder particles and those of the boundary phase in the ceramic.

The significance of surface activity for BaTiO₃ powders (0.01-μm particle size) was illustrated by the frequency dispersion of the dielectric properties. Fine-sized powders tend to absorb gaseous species because of their large surface-area-to-volume ratio. The dielectric measurements indicated a surface layer of adsorbed water was removed by an isopropanol wash. The effect of
water vapor on the dielectric behavior of larger sized powders was less significant. The data indicated that on removal of adsorbed water, there was no significant difference in the relative dielectric constants of fine and coarse particle size BaTiO₃ powders. Removal of surface water by isopropanol washing reduces the dissipation factor, which is important in processing thick-film capacitors.

These results indicate that the previously reported particle-size dependency of dielectric constant of BaTiO₃ powders is not an intrinsic, surface-layer characteristic, but is primarily due to the difference in surface reactivity or degree of hydroxylation caused by varying surface-area-to-volume ratios. Further, it seems that a particle-size dependence does not exist for “clean” surfaces. This work clearly identifies one of the problem areas where improvements can be made in capacitor materials.

To furnish a wider variety of dielectric materials for thin-film capacitor applications, Marshall Space Flight Center sponsored an experimental program on thin films of oxides (ref. 143). Thermally evaporated oxides of yttrium, scandium, vanadium, lanthanum, cerium, praseodymium, neodymium, samarium, gadolinium, dysprosium,holmium,erbium, and ytterbium were measured at 300° F for their dielectric properties, at 75 V. Dielectric breakdown strengths in excess of $5 \times 10^6$ V/cm were observed. Relative dielectric constants measured from 2 to 22 and capacitances were as high as $156 \times 10^{-9}$ F/cm². The oxides of cerium, lanthanum, neodymium, gadolinium, praseodymium, and erbium showed the greatest promise. Cerium oxide evaporates with relative ease and had the highest dielectric constant. Lanthanum oxide was slightly more difficult to vaporize but showed a tremendous dielectric strength (approximately $8.7 \times 10^6$ V/cm) and very good capacitance. Neodymium oxide had a dielectric strength of $3.4 \times 10^6$ V/cm; gadolinium oxide, $3 \times 10^6$; praseodymium oxide, $3.2 \times 10^6$; and erbium oxide, $4.7 \times 10^6$. The maximum dielectric constants of these same oxides were, respectively, 11.8, 8.2, 12.1, and 3.5.

One of the problems in electrolytic capacitors is the lack of a high dielectric constant film. Electrolytic capacitors are able to produce high capacity in a small volume by virtue of thin, high-quality films on supporting thin, flexible metallic electrodes. These may be then rolled or stacked to yield high-volume efficiency. The principal films used commercially are anodized aluminum oxide and tantalum oxide. Their dielectric constants are 9 and 20, respectively. A large increase in capacitance per
unit volume could be achieved if the dielectric constant could be increased even partially toward the level of the ferroelectric ceramic materials, whose dielectric constants range into the thousands.

A program was sponsored by NASA Headquarters at Lockheed Missiles & Space Co. in which several approaches toward the formation of high dielectric constant materials in thin-film form by electrolytic techniques were considered (ref. 144). The emphasis was on barium titanate, with some attention being devoted to zirconates, niobates, and tantalates. Besides barium compounds, comparable calcium, magnesium, strontium, and potassium double oxides were evaluated.

The basic approach was anodization of the refractory metal with simultaneous deposition or occlusion of the second oxide in the anodized film. Aqueous electrolytes, organic electrolytes, and gas-phase systems were utilized. Molten-salt systems were not used because of excessive solubility of product oxide materials.

The dielectric films produced yielded properties that were equivalent or slightly improved over simple anodized films. In the case of titanates and niobates, films were produced with an order of magnitude improvement of capacitive properties and a consequent improvement in loss and resistive properties by a subsequent vacuum heat treatment coupled with an air oxidation or healing step.

Lewis Research Center has worked on high-temperature capacitors for use in space power conditioning units. An experimental program was begun because capacitors presently available from commercial sources have limited maximum operating temperature (up to 700° C); they are usually bulky and have high electrical losses at elevated temperatures (ref. 145). Four high-purity materials were investigated: pyrolytic boron nitride (PBN), single crystal alumina (sapphire), hot pressed beryllium oxide, and polycrystalline alumina. The results showed the PBN to have superior electrical properties under testing conditions and the capability of being fabricated into thin (0.001-in.), large-area wafers.

The significance of this work lies in the high-voltage application of dielectrics at extremely high temperatures where conventional commercially available materials cannot function. As higher operating temperatures and voltage gradients are applied in microelectronics, the materials and techniques in this program may be applied.

A basic research program to relate empirical factors of cations
with ferroelectric transition temperatures was sponsored by NASA's Electronic Research Center at the State University of New York at Stony Brook (ref. 146). The program was to study the dielectric properties of ceramic mixed crystals containing barium sodium niobate, \( \text{Ba}_2\text{NaNb}_5\text{O}_{15} \), of the tungsten bronze structure, to correlate the "intrinsic" dielectric properties with the chemical composition and the microstructure of the samples and to improve the dielectric properties. As a result, it is now possible to calculate the ferroelectric transition temperature for such niobates with substitution of cations of alkalis, alkaline earths, lead, and lanthanum. Such work can lead to a better understanding of basic mechanisms and is essential in tailoring capacitor properties to specific NASA and industrial needs.

Over a period of several years, R. C. DeVries and others in the NASA-sponsored university program at the Interdisciplinary Materials Laboratory at Rensselaer Polytechnic Institute studied properties of high-purity, single-crystal and polycrystalline barium titanates. Among the subjects studied were: (1) methods to grow single-crystal barium titanate (ref. 147); (2) measurements on the refractive index (ref. 148); (3) single-crystal domain motion (ref. 149); and (4) dielectric aging and microstructure in barium titanate (ref. 150), and in the barium titanate/calcium titanate systems (refs. 151 and 152). This basic work may later be applied commercially.

The NASA contributions described above were primarily on individual materials and discrete capacitors. In chapter 5 on microcircuitry, other contributions pertinent to the use of capacitors in circuitry are cited. The technology transfer resulting from NASA contributions is appraised in chapter 6.
Ceramics and Glasses in Microcircuitry

The commercial success of the transistor made the rewards of microcircuitry apparent. Previously, active devices were large and consumed large amounts of power. As a result, there was an uncompromising need for passive components (capacitors, resistors, and interconnections) to be large to handle the power requirements for tubes, relays, etc. The passive components were relatively small and consumed slight power compared to the active devices, and there was little need to miniaturize or to consume less power. The situation changed with the rise of semiconductor technology. Active components then became small in comparison to passive components, and consumed much less power than the tubes they superseded. The reduction in size and power consumption of passive components, therefore, became an important goal in circuitry. Miniaturization of discrete components has been pursued, but the advent of microcircuitry is a response to the need for extraordinary techniques to produce even smaller capacitors, resistors, interconnections, and, consequently, total circuitry.

Work on microcircuitry has also increased the reliability of circuits and decreased costs. The former benefit has been accomplished by inherent solid-state reliabilities, a stable reliable active device, the reduction in the number of steps in producing a circuit, better control of processing and materials, improvements in quality control and proof testing, and redundancy. The complexity of modern electronic systems has required increased reliability. With poor reliability, maintenance costs and excessive downtime would preclude complicated devices such as computers.

The complexity of modern electronic systems with vast numbers of circuits also necessitates a low unit cost per circuit. If this requirement were not met, the initial capital cost could prevent economical application of potential laborsaving devices or even prevent the development of electrical devices offering unique capabilities. With increased reliability and low costs, electronic
systems can be used to perform new functions and to replace costlier, bulkier, or less reliable machinery.

The components used in microelectronics have evolved from electrical and electron-tube applications. However, unique requirements are placed on components by each of the microelectronics technologies, so different compositions, processing, and configurations have evolved for each of the three main microelectronic technologies: thick-film hybrid, thin-film hybrid, and monolithic integrated circuitry.

In thick-film hybrid circuitry, individual screen printing processes are used to lay down conductor, resistor, capacitor, and insulator pastes onto substrates. The pastes contain a minor proportion (10 to 20 wt %) of glassy bond. On heating, the pastes fuse into glass-bonded components which become an integral portion of the substrate. Active elements, inductors, and more critical passive components are then bonded to conductor mounting pads which are reserved for their inclusion into the circuit. Access to the circuitry is provided by external leads or conducting pads at the edges of the substrate. Depending upon the requirements of the circuit, it is (1) sealed in a hermetic package, (2) given an organic conformal coating to protect it from mechanical abuse and environmental degradation, or (3) included in a larger circuit where (1) or (2) is performed.

In thin-film hybrid circuitry, vacuum evaporation, chemical vapor deposition, or sputtering are used with photolithographic processes to lay down conductors, resistors, capacitors, and insulators. Two processes are followed: (1) additive—in which the film layers are deposited through masks; and (2) subtractive—in which all the layers are deposited, and then patterns are selectively etched. The remaining steps in processing are very similar to those of thick-film hybrid circuitry except for connections to the circuit, which require different processing materials.

Monolithic integrated circuitry involves the control of the electrical properties of carefully prepared single-crystal wafers of silicon by diffusing minute amounts of impurity elements into the silicon in controlled locations and amounts (ref. 153). Two types of impurities are used. One addition causes the formation of excess electrons (n-type silicon), while the other causes the deficiency of conduction electrons (p-type silicon). The boundary region between the different types of silicon is called a p–n junction. It is possible to make a single junction that performs as a diode or as a voltage-dependent capacitor. Using two junctions, a transistor may be formed. A resistor is made by electrically
isolating the silicon with a $p-n$ junction. An alternate approach is to use high-resistivity, thin-film resistors directly on the surface of the silicon chip. Connections between the various circuit elements on the silicon wafer can be made through the silicon or by an overlay metal pattern. Connections to the silicon wafer can be by tiny wires, or by bumps of conductor material bonded to conductor pads, or by beam leads extending from the sides of the wafer. In the latter two techniques the connecting procedure also provides mechanical support and thermal cooling paths. Final passivation and packaging involve similar techniques.

The remaining sections of this chapter describe the ceramic- and glass-based components in each of the three microelectronic technologies and in packaging.

CERAMICS AND GLASSES IN FILM TECHNOLOGIES

The use of ceramics and glasses in film technologies is centered in three areas: substrates, passivation layers, and crossovers. Ceramic resistors and capacitors including film types were covered in chapters 3 and 4.

Substrates

Many materials have been proposed for substrates, but ceramics and glasses are by far the most widely used (refs. 154 to 160). Competitive materials include dielectric-coated metals (ref. 161), plastics, and single crystals such as quartz, sapphire, beryllia, and spinel. Glasses and ceramics predominate because they possess the best combinations of important properties. Requirements include

1. Flatness
2. Smooth surfaces
3. High strength in thin sections
4. High thermal conductivity
5. Thermal stability
6. Chemical durability
7. High electrical resistivity and low dielectric loss
8. Low coefficients of change with temperature or frequency
9. Availability in a range of sizes and shapes
10. Compatibility with films and their processing
11. Inexpensiveness

The requirements sum up as the ability to take power loading without shorting, control over film processing and properties, and reliable component performance.

Requirements such as strength and thermal conductivity must be suited to the films to be applied and are usually variable as the
user tries to get the most advantageous value within acceptable costs. Virtually all ceramics and glasses have minimum acceptance values for these properties. Flatness, surface finish, chemical stability, and thermal stability must be at certain minimum levels before a substrate can be used in a given process. For example, thin-film vapor deposits require smooth, clean surfaces to minimize flaws; so a glass, a glazed ceramic surface, or an exceptionally fine-grained ceramic is necessary (ref. 162). A high degree of flatness is also required for the photolithographic techniques. Since a very clean surface is demanded, the substrate must be compatible with the cleaning procedures, as well as resistant to attack by etching solutions. For screen printing of thick films, flatness as measured by camber becomes important in high-speed production.

Substrates for thick films have included alumina, beryllia, barium titanate, forsterite, steatite, or glass. Most widely used currently are alumina ceramics. The 96% alumina formulation has a combination of the most desirable properties with respect to thermal conductivity, thermal expansion, and strength at a relatively economical price. Beryllia is used in applications where highest thermal transfer is required and a greater ratio of cost relative to alumina is justified. The more complicated the design of the substrate, the less the relative costs of the starting particulate materials will matter in the price of the finished substrate because the labor costs then become the dominant factor. Steatite, forsterite, and barium titanate were used where screen-printed carbon film resistors were applied prior to the large-scale adoption of cermet resistor films. Barium titanate is also used because it provides a second function as a capacitor dielectric and has been common for years in resistor-capacitor networks. Steatite and forsterite are less costly than alumina and easier to machine, which makes them attractive when production costs are important. Glass is widely used as a substrate and is restricted to low power applications because of two limitations: poor thermal conductivity and low strength. Important substrate properties are compared in tables X and XI of chapter 3.

Surface profiles for glasses, glass ceramics, and ceramics (ref. 163) are shown in figure 22. It is apparent from these curves that glasses exhibit surfaces that are smoother than the ceramics. A surface finish for 96% alumina made by the tape process is 8 to 10 μin. as fired and 1 to 2 μin. as polished. Camber of alumina substrates is on the order of 0.003 in./in. as fired and by selection can be as low as 0.001 in./in. Glasses provide less than 1-μin.
Fig. 22.—Surface profiles of substrate materials: (a) Drawn soft glass sheet. (b) High-density alumina, ground and polished. (c) Photosensitive glass, polished. (d) Photosensitive glass ceramic, ground and polished. (e) High-density alumina, as fired. (f) Photosensitive glass, processed. (g) Photosensitive glass ceramic, as fired. The distance scale along the surface (the abscissa) is the same in all figures, but the surface height scale (the ordinate) is larger in (e), (f), and (g). Note: 125 Å is equivalent to 0.5 μin.

finishes, as do glazed ceramics. Nevertheless, a good deal of research is going into unglazed alumina substrates to develop a better as-fired surface finish because of their other advantages. They have better thermal conductivity than glazed substrates. In general, the surface finish requirement for thick films is satisfied by the 96% or higher alumina ceramics. Thin-film technol-
ogy has so far required glass, glazed ceramic, or higher purity ceramics (99+% Al₂O₃ or BeO) with fine-grained, low-porosity microstructures. Reasons for the extra quality demanded of surfaces for thin films include their smaller thicknesses and ability to maintain a 1-mil line spacing versus, at the best, 8 mils for thick films. As a result, a requirement for fewer and smaller defects exists.

High strength in a substrate material contributes greatly to reducing handling problems. The substrates will sustain rougher handling; they can be made thinner in larger surface areas, or in more complex shapes; they will withstand high thermal gradients; and they will bond with components having greater thermal expansion mismatch. The high strength of some substrates, however, has posed a problem; so substrates with perforated or grooved patterns are made which facilitate the breaking of large multiple unit substrates into smaller individual ones. Diamond scribing and laser sawing are alternate techniques.

High thermal conductivity in substrates also contributes greatly to the ease of processing circuits. The substrate may be heated quickly to higher temperatures without fear of fracture due to thermal gradients, and temperature equalization is readily achieved. Cooling can also be done quickly and uniformly. In service, high thermal conductivity of a substrate enables lower operating temperatures or the use of higher power without overheating the circuit elements and causing property drifting. This behavior is shown in figure 23, where the superiority of a glazed alumina substrate over a glass one is clear (ref. 164). Equalization of temperature for the circuit elements is also more nearly achieved, which prevents components from varying in properties due to temperature differentials.

Stability at high temperatures and in various chemical environments is required if a substrate is to be adaptable to the processes of circuit deposition. In thick-film processing, temperatures as high as 1600° C in a wet hydrogen atmosphere might be needed if a technique such as the molybdenum-manganese metallizing process is used. Or the substrate must be able to resist harsh chemical-cleaning techniques that are needed for uniform, adherent films. The evaluation of the surfaces for cleanliness has required extensive research (ref. 165).

High electrical resistivity and low dielectric loss are needed in substrates, since one of their primary functions is to electrically isolate circuit elements. Ceramics and glasses at room temperature have high resistivity, which decreases exponentially
with heating. Low dielectric loss is necessary to reduce heating, especially at high frequencies, and to minimize dielectric breakdown. The ceramics are superior to glasses in this regard, since they show lower conductivity at higher temperatures. A troublesome problem is the diffusion at high temperatures and electrical fields of alkali ions in silicate-containing glasses or in the glassy phase within polyphase ceramics. Figure 24 shows the percentage of resistance change for glasses containing sodium oxide and glazed alumina for excessively high power loading as a function of time (ref. 164). The higher thermal conductivity of the alumina allows the resistors to remain at lower temperatures and reduces drift.

Low sodium-containing materials or compositions that impede the mobility of \( +\text{Na} \) ions can be critical in many applications. Surface resistivity is another important consideration, since ad-
sorbed or chemically formed films on surfaces can drastically increase conduction between circuit elements on a substrate. Well-made, fully reacted, homogeneous substrates greatly reduce the occurrence of unwanted adsorbed surface layers, and aid cleaning.

Compatibility of deposited films with substrates is dictated by thermal expansion matching, chemical interaction, and ability to withstand processing conditions. The thermal expansion of films used with substrates varies from 0.5 to $14 \times 10^{-6}$ in./in./°C, and if two different types of films are used on one substrate, ideal thermal expansion matching is precluded (ref. 166). The temperature at which films adhere is important in determining the total strain between films and substrates. For adequate bond strength the substrate must form chemical bonds with the film, so some degree of chemical interaction is necessary. However, excess reaction will cause modification of the film and loss of properties. The ability to withstand processing conditions is, of course, required and this usually means chemical stability at high temperature under varying atmospheres and contacting materials.

Ceramic substrates can be formed in a number of ways. Though simple die pressing is practiced, current favorites are doctor blading, casting, or a number of extrusion techniques (refs. 167 and 168). With these techniques, thin, flexible, plas-
tic-bonded sheets or “tapes” are made that may be stamped or drilled prior to a firing operation. During the firing the organic additives are expelled and the ceramic is sintered to maturity. Final polishing or glazing may be done to improve the surface characteristics. Substrates are made of relatively high purity materials, especially of unusually low alkali content. For glass substrates, the melt is prepared by the careful techniques developed for optical glass so internal and surface flaws are minimized. For substrate applications where a rapidly cooled, thin ribbon of glass may be adequate for production, glass formulations may be used that could not normally be prepared without crystallization.

The sheet technology has been extended to “transfer tapes” in which a thin sheet of material is attached to a plastic carrier film. The material is then transferred from the film to a desired surface by an adhesive layer which is activated by pressure. During the subsequent firing operations, the organic binders are completely pyrolyzed and a uniform coating is formed. This technique may be used to apply glazes (ref. 169), conductors, metallizing, resistors, and dielectrics to a variety of materials.

For thin-film applications, very smooth surfaces are needed for certain film components but a rougher surface may suffice for others. A selective glazing technique has been reported in which the same substrate was used for capacitors requiring glazed surfaces and for resistors that could tolerate the un glazed surface (ref. 170). The resistors can also operate cooler with the higher heat-conducting, unglazed surfaces.

For epitaxial growth of thin films, single-crystal substrates are used that have crystallographic characteristics similar to those of the desired film. Silicon homoepitaxial deposition on silicon is very straightforward, but silicon can also be heteroepitaxially grown on single-crystal sapphire, spinel (ref. 171), quartz, or beryllia. As an example, silicon, which has a diamond cubic structure, grows on the (1124) face of sapphire, which is hexagonal, in the (111) orientation. For silicon epitaxy, a model has been suggested which assumes a fit between the silicon and the metal-ion sites in the metal-oxide substrate and a probable bonding of the silicon by the oxygen lattice (ref. 172). Work has also been described in which sapphire is used as the substrate for a heteroepitaxial semiconductor technology at microwave frequencies (ref. 173). A project is in progress to determine whether GaAs single-crystal films can be developed on transparent glass-ceramic substrates (ref. 174). One approach is to cause
oriented crystalline growth in the substrate to provide arrayed nucleation sites.

To achieve a high density of components, more interconnections between components on a substrate and of input/output leads are often necessary. An overall view of this problem by Wilcox and Sands (ref. 175) states that an extension of the historical role of the substrate as a mechanical supporting and environmental protecting medium is required. Additional functions include interconnections, power distribution, thermal cooling paths, and input-output leads. The circuit designer accomplishes his goals by stressing circuit density, electrical signal transmission characteristics (ref. 176), voltage drops, and thermal dissipation. He is limited in accomplishing his goals by constraints that appear in substrate technology such as lead reduction, geometry, dielectric constant of the insulating material, lead electrical conductivity, and thermal conduction of the substrate and exiting leads. The results of the design are then achieved in terms of cost, performance, and reliability, as depicted in figure 25.

One approach to increasing the component density is the use of multilayer substrates, which contain internal conductor networks

![Diagram of design requirements and technology constraints](image)

**Figure 25.** Basic packaging considerations in terms of design requirements, technology constraints, and packaging results.
with input/output terminal at the substrate surface. Advantages of this approach may be (ref. 177) :

1. The layer of dielectric isolation is many times thicker than that obtained by thin- or thick-film techniques
2. Good physical strength
3. Precise layer registration
4. Ability to use the surface in the same manner as standard substrates

Several techniques have been used to build acceptable structures. One utilizes noble metal interconnections buried in 96% alumina ceramic, and enables a wide variety of subsequent processing operations; i.e., thick film, active metal, evaporated thin film, etc. (refs. 177 and 178). A buried conductor sheet resistivity of $7-10 \times 10^{-3}$ $\Omega$/sq is quoted (ref. 177). A second type uses 99% alumina as a ceramic with porous molybdenum metal forming buried conductor channels. These channels are subsequently filled with copper in a final operation that involves a "capillary-fill" technique. A buried conductor sheet resistivity of $5 \times 10^{-4}$ $\Omega$/sq was achieved with this technique (ref. 179). Figure 26 sketches one multilayer construction (ref. 177).

**Crossovers and Passivation**

In the construction of film circuits or monolithic circuits having high densities of components, it is unavoidable to have conductors crossing over each other. The function of crossovers is to provide a low-loss, low-capacitance insulation between conductors. A number of techniques are available to do this. In the previous section, the use of multilayer substrates was mentioned. Insulating films and chip insulators with conductive patterns that cross conductors or wires are other approaches. The passivation of circuitry is the use of films that cover and protect circuit elements from the influence of each other or from harmful external environments. Film crossovers and passivation layers will be described first, and chip insulator crossovers and wire crossovers will be considered later.

For thick films two types of crossover films are used commercially. One is completely glass, while the other is a crystallizable glass. As an example (refs. 179 and 180), a glass is available that has a dielectric constant of 7 to 8 and a dissipation factor of 0.006. Typically, two 20-mil-wide conductors crossing at right angles and separated by the crossover glass will show a capacitance of 2.0 pF, and an insulation resistance of $2 \times 10^{13}$ $\Omega$ with a breakdown voltage over 250 V. For this type of crossover it is neces-
Figure 26.—Representative multilayer ceramic circuit board showing the features of the various layers; general purpose for four digital IC's.
sary to make separate firings of the conductive layers and the
crossover glaze, in order to prevent sinking (shorting of the con-
ductors) and swimming (lateral translation of the conductors).
Each successive film is fired at a lower temperature than the one
below it.

To overcome these difficulties, crystallizable glaze crossovers
have been developed (refs. 181 and 182). These compositions,
when fired, produce translucent films with dispersed ceramic
crystals in a glass matrix. A dielectric constant as low as 10 to
15 and a dissipation factor of less than 1.5 percent at 1 kHz is
possible. Improvement in printing resolution and reduction of
pinholes or shorts is claimed. The major advantage of this se-
ries, however, is that once fired (at approximately 850° C), the
material does not resoften unless heated well above that tempera-
ture, and separate firings of conductors and crossover films are
not required. A disadvantage is the higher dielectric constant of
the crystallizable film.

Usually, thick-film resistors, capacitors, or conductors do not
need to be passivated, as they are self-encapsulating. However,
resistor encapsulants are used in cases where extreme environ-
ments (such as water filming or reducing atmosphere) are en-
countered, or for protection against reactive organic encapsulants
and potting materials, and for protection against overspray in
resistor trimming with the air abrasion technique. One commer-
cial encapsulant (ref. 183) is fired at 500° C for 1 to 2 min at
peak temperature and produces a matte, semitransparent film.
A change in resistor value of less than 3 percent is typical when
using the encapsulant.

For thin-film technology, a wide variety of insulators and cross-
overs (ref. 184) are available. A description of insulating thin
films has been given in chapter 4, where an alternate use as
dielectrics in capacitors is described.

To reduce losses and capacitance coupling between conductors
crossing each other, it is desirable to have an airgap between
them. Crossover wires, beams, and chips accomplish this. Cross-
over wires were the first technique used to interconnect integrated
circuits and join them into hybrid circuits, and they are still widely
used. Gold wires are prevalent because of their flexibility, non-
corrosive behavior, and good conductivity. Often they are
connected to aluminum contact pads. The advantages in wire
interconnections are design flexibility, low losses, and low capaci-
tance. Wire interconnections, however, have at least two draw-
backs: attachment of wire leads is expensive because of the labor
involved, and connections require careful process control for reliability. The use of gold-aluminum contacts has the hazard of "purple plague," which is a formation of \( \text{AuAl}_2 \) at the interface. In the presence of silicon, an additional compound, \( \text{Au}_2\text{Al} \), forms, which is fragile, a poor conductor, and believed to cause defects (ref. 185). To avoid this problem, some manufacturers are using all-aluminum systems with aluminum wires and pads (ref. 186) or all-gold systems.

Crossover beams are interconnections developed for hybrid thin-film circuits. They consist of free-standing metal structures made by photolithographic techniques. The preparation of a crossover beam is shown schematically in figure 27 (ref. 187). A beam of this type offers the advantage of air insulation with low losses and low capacitance.

A recent approach to the problem of conductor crossovers is the use of chips as crossover bridges on substrates. In one example, a glazed ceramic substrate is prepared with aluminum bumps 0.2 to 0.3 mil in height mounted on the conductors at the crossover sites. A silicon chip which has the desired aluminum conductor crossover pattern is then bonded face down onto the substrate in the same manner as a flip chip. As an example, a circuit of 16 face-bonded integrated circuits and 18 crossover chips was prepared in a 1- by 1-in. package and contained over 300 individual conductor crossovers. Using this approach, it was not necessary to use an alternate three-tier multilayer substrate technique. A comparison of this approach to thick-film and multilayer ceramic techniques is shown in table XX (ref. 188).

An extensive survey of chip-joining techniques has been described by Miller (ref. 189), and a survey specifically on flip-chip bonding systems has been made by Meyers (ref. 190).

**CERAMICS AND GLASSES IN MONOLITHIC INTEGRATED CIRCUITRY**

The preparation of conventional double diffused transistors, the newer metal-oxide-semiconductor (MOS) transistors, other devices, and integrated circuits require the use of ceramic and glass insulating films. For example, a conventional planar transistor in an integrated circuit is made by selectively diffusing impurities into a slice of silicon, using silicon oxide as a diffusion mask (ref. 191). Once the emitter, base, and collector regions have been created, an insulating layer of silicon dioxide is formed over the surface, and the metal contacts are deposited. Silicon dioxide, however, is susceptible to the diffusion of alkali ions at elevated conditions.

**Figure 27.—Crossbeam preparation using photolithographic techniques.**
1. Prepare Gold Conductor Pattern

2. Deposit Copper Spacing Layer

3. Define Support Columns

4. Define Crossover Span

5. Electroplate Crossover Structure

6. Produce Free Standing Crossover
### Table XX.—Comparison of Crossover Chip Technique and Multilayer Ceramics

<table>
<thead>
<tr>
<th>Design criteria</th>
<th>Multilayer ceramics</th>
<th>Aluminum crossover chip technique</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Line width:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Surface, in.</td>
<td>0.005</td>
<td>0.004</td>
</tr>
<tr>
<td>Buried, in.</td>
<td>0.010</td>
<td>NA</td>
</tr>
<tr>
<td><strong>Line spacing:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Surface, in.</td>
<td>0.005</td>
<td>0.002</td>
</tr>
<tr>
<td>Buried, in.</td>
<td>0.010</td>
<td>NA</td>
</tr>
<tr>
<td><strong>Riser holes:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diameter, in.</td>
<td>0.010</td>
<td>NA</td>
</tr>
<tr>
<td>C-C spacing, in.</td>
<td>0.030</td>
<td>NA</td>
</tr>
<tr>
<td><strong>Resistivity:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Surface wiring, Ω/sq.</td>
<td>0.007</td>
<td>&lt;0.003</td>
</tr>
<tr>
<td>Buried wiring, Ω/sq.</td>
<td>0.010</td>
<td></td>
</tr>
<tr>
<td>Crossover capacitance, PF</td>
<td>&lt;1.0</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>Chip density, 1- by 1-in. substrate</td>
<td>X (max)</td>
<td>&gt;2X</td>
</tr>
</tbody>
</table>

NA = Not available.

Temperatures and voltages. To avoid this problem, a layer of amorphous or glassy silicon nitride, which is much more imperious to alkali ion diffusion, can be deposited onto the silicon by chemical vapor deposition. Bell Telephone Laboratories (ref. 192) and others (ref. 193) have utilized this process to seal critical junction regions and eliminate the need for hermetically sealed packaging. Bell Telephone also developed "beam lead-sealed junction" technology that enables the formation of transistors and integrated circuits which may readily be joined into film circuitry (ref. 162). Heavy gold leads that extend from the edges of the device much as a beam would extend from a building to support a roof overhang are constructed by photolithography. A pictorial view of a beam lead-sealed transistor is shown in figure 28 (ref. 192). In this system the silicon dioxide-silicon nitride layer passivates the semiconducting silicon from the environment.

In forming MOS transistors, layers of oxides of silicon are also used in the processing and in the devices (ref. 191). A thin layer of phosphosilicate glass is used for passivation in the example shown. This technique has been employed for device passivation (ref. 194) and has been theoretically analyzed (refs. 195 and 196). Silicon nitride or phosphosilicate glasses can be used for final passivation or encapsulation for conventional transistors, MOS transistors, other semiconductor devices, or integrated circuits. Both techniques satisfy the requirements of total protection from
Gold collector beam lead
Gold base beam lead
Silicon dioxide-silicon nitride
Gold emitter beam lead
Emitter (n)  Base (p)  Collector (n)

**Figure 28.**—This cutaway drawing shows the basic structure of a beam lead sealed junction transistor. Part of the emitter electrode and beam lead, along with the underlying material, is removed to show the contact areas of the emitter and base electrodes. The collector is in the n-type silicon.

the environment but offer little protection from mechanical shocks or abuse. Silicon nitride has the disadvantage of slow etching rates, which hampers its wide adaptation for integrated circuitry. The phosphosilicate glasses have the disadvantage of a tendency to hydrolyze.

**PACKAGING**

Once a microcircuit has been prepared and tested, it may have to function in its designed modes under widely varying conditions and environments. Protection of circuitry in such cases is the province of "packaging." For many applications, molded plastic or conformal coatings are acceptable. However, these coatings do not provide hermetic seals as they are slightly permeable to oxygen, water vapor, and other contaminants. For hermetic sealing, packaging systems are based on metallic or inorganic systems. The package must perform a number of functions and meet tough electrical, chemical, mechanical, and radiation requirements (refs. 197 and 198).

Electrical requirements for the package are to provide a means of carrying sufficient currents and voltages between external sources and specific regions in the interior. The isolation might include inductive, capacitive, as well as conductive coupling. The package must also provide a path for the flow of heat away from
the device within to prevent overheating. If the power dissipation of the device exceeds the ability of the package to remove the heat, cooling fins or a stud-mounted heat sink must be employed.

Chemical isolation must be provided so that the interior provides an environment compatible for device performance and reliability. Under normal conditions oxygen, moisture, and air pollutants must be excluded, although severe extraordinary conditions may also be faced. Electrochemical effects such as electrolytic corrosion must also be considered.

Mechanical requirements dictate that the package be sufficiently strong to allow the entire structure to withstand the stresses occurring during and after assembly, during connections to other systems, and in use. The stresses might include frequent bending of leads, dropping, etc. Mechanical properties may limit temperature, thermal gradients, and pressures to which the package can be subjected. The ease of handling and flexibility of manufacturing processes in joining the package in larger arrays is also affected by mechanical properties. They also determine space requirements for the package and of the final system.

For some applications, radiation considerations may be important. In such cases the package may have to isolate the device or circuit from light or other external radiation. The reverse may also be required where the external circuit may have to be isolated from the interior radiation effects. The package may have to provide a shield against external magnetic fields or may be needed to provide a path for magnetic flux.

A number of packaging concepts have been developed for transistors, integrated circuits, and hybrid circuits. One concept is the encasement of the individual components in a ceramic, plastic, or metal container. These may be individually sealed or merely mounted for handling and attachment ease. As an example, one supplier has developed a line of miniature packaged diodes and transistors for insertion into any type of microcircuit: printed circuit, thick-film, or thin-film construction. These active elements are contained in ceramic packages 0.060 by 0.050 by 0.035 in. in size and can be soldered into place. These "chip blocks" are extremely rugged and may be replaced in the same manner one would replace standard discrete components in a circuit board. Figure 29 shows a number of chip-block diodes on a human finger.

Ceramics are also used as "carriers" for active devices in many hybrid designs. In this application, tiny active chips are bonded to larger ceramics metallized with a conductive pattern. The carrier provides support and mechanical strength to the active
device, acts as a heat sink, and is an intermediary in increasing the size, dimensions, and spacing of electrical contacts. The ceramic is also amenable to automated production processing. The ceramic shape can be a flat plate, a channel design, or whatever configuration is necessary to provide a means of utilizing active chips in hybrid circuits. An example of the versatility in design that is possible is a transistor cup mount used by a major television producer (ref. 199). The carrier is round and pill shaped with
four distinct levels, each for a specific purpose: the lower level for chip bonding, the tread level for wire bonding, the third level for containing potting compounds, and the fourth level for external land connections. A flat on the periphery allows high-speed automatic feeding and orientation. This carrier can also be used as a crossover jumper of up to three leads of 0.015 in. with 0.015-in. spacings. Carriers must be sealed with other hybrid circuit elements as they do not provide environmental protection.

Types of hermetically sealed packages commonly available include: transistor outline (TO) cans, flat packs, dual-in-line flat packs (DIP), and covered substrates (refs. 200 and 201). TO cans were first introduced to provide packaging for transistors. Their shape was adapted for that need with a flat, flanged base or "header" and a cup-shaped cover. The header consists of a metallic ring, usually of Kovar,® encircling a glass base with Kovar pins inserted through the glass base near its periphery. Internal connections are usually wire bonded.

The first microcircuits were packaged in TO-can construction with redesigned low covers. A typical construction is shown in figure 30 in a sectional view for a 10-pin design (ref. 202). As the microcircuits increased in size and complexity, the diameter of the TO can and the number of leads were increased.

“Flat packs” were specifically designed to match the geometry

![Figure 30](image)

**Figure 30.** Components assembled in TO-5 package.

®Registered trademark of Westinghouse Electric Co.
and electrical contact needs of microcircuits. In the flat-pack design, leads are brought out of the walls of the package and, as a result, a greater number may be accommodated than in the TO-can designs. A variety of combinations of glass, ceramic, and metal is used. Three major groups exist: (1) packages which have a ceramic or metal base and lid and an all-glass wall; (2) packages which have a ceramic wall, base, and lid; and (3) packages which have a glass base and wall and a glass, ceramic, or metal lid. Choices between the above types are made on the basis of electrical, mechanical, thermal, and cost requirements. The glass-walled package (group 1) is relatively economical, has good lead density, and with a ceramic or metal base can dissipate considerable heat. It has the disadvantage of requiring the assembly of a minimum of four pieces. The all-ceramic construction (group 2) is rugged, has good design flexibility and can dissipate considerable heat, especially if the base is made of beryllia. Group 3 is economical and easily assembled, since a minimum of two parts may be used. The principal disadvantages are poor heat dissipation and low ruggedness.

A typical commercial flat package (ref. 203) of all ceramic design is shown in figure 31. The length is 0.320 in., the width 0.250 in., and the thickness from 0.030–0.070 in., depending on the design. The metallization pattern on the base can be varied to meet internal connection needs. Therefore, internal connections can be by wire bonding, by the flip-chip technique, or by the beam-lead technique.

The dual-in-line flat package configuration mates integrated circuitry to printed circuit boards. It has the flat package design with leads existing through the walls, but the leads are bent 90° and extend below the base. With this design the dual-in-line leads may be inserted into printed circuit boards. Soldering of leads may then be done by dip or wave soldering on the bottom side of the board. Dual-in-line packages have been made of both plastic and ceramic and an example is shown in figure 32.

In the case of ceramic dual-in-line packages, the leads are embedded in the package sealant, the sealant producing a hermetic seal around the leads and between the lid and base when subsequently fired at sealing temperature. Properties of ceramic package sealants are given in chart form in chapter 2, table VIII.

Flat-form packages provide a strong illustration of a development for space needs coming into wide usage for civilian equipment. Originally developed for critical, size-limited applications in tracking, guidance, and programing systems for defense and
USE OF CERAMICS IN MICROELECTRONICS

\[ \text{FIGURE 31.—Commercially available all-ceramic flat package.} \]

\[ \text{FIGURE 32.—Semiconductor integrated circuit—dual-in-line package.} \]
space exploration to permit full realization of the high component
density inherent in monolithic integrated circuits, they are now
widely used in data processing and industrial-control equipment
and are appearing in consumer appliances.

Some of the latest trends involve the use of a ceramic substrate
as the base of the hermetic package with a metal or ceramic
cover. A seal may be made along the edges and leads are brought
out through the base. Low-cost plastic encapsulation of micro-
circuits is being done when practical. Such encapsulation (ref.
204) provides protection from contamination during handling
in fabrication and by fungi and airborne foreign matter in ser-
vice. Encapsulation also provides a protection against periods
of high moisture and coatings can be used to anchor components
to circuit boards.

NASA CONTRIBUTIONS

NASA has made many contributions to the use of ceramics in
microelectronics, including new designs in microcircuitry, new
film-preparation techniques, and information transfer.

New Designs in Microcircuitry

Since 1962 there has been a strong microelectronics thick-film
program at Langley Research Center. This work has been cen-
tered in the Microelectronics Section, Telecommunications Re-
search Branch, Flight Instruments Division. Work in this group
has been motivated by the need for small, high-reliability com-
ponents for flight projects. Much of this work has been on ma-
terials research, and portions have been mentioned in the sections
on resistors and capacitors. In this section, system applications
will be described, bringing out the engineering considerations and
the advantages gained by utilizing the thick-film hybrid micro-
electronics approach.

Thick-film hybrid circuits have been used in a microelectronic
instrumentation system for scaled aircraft models at Langley Re-
search Center (refs. 205 and 206). To acquire aerodynamic
information from aircraft models in ground wind tunnels, data
from sensors in the models are transmitted along wires to record-
ing stations. For certain types of dynamic testing where buffet-
ing and fluttering is caused by controlled gust conditions, the
model must be freely suspended and remotely controlled. These
requirements preclude the normal thin, rigid supporting rod which
would dampen vibrations; only thin, flexible connecting wires to
control and monitoring stations may be used.

As a result, it was necessary to construct modelborne micro-
circuitry that could amplify and synchronize the data for trans-
mission along a thin, light instrumentation cable and not adversely affect the model's aerodynamic response.

The instrumentation had to have these features:

1. Since the tunnel atmosphere was Freon, all routine trimming of the model aerodynamics and onboard electronics had to be remote and active during an experiment.

2. Data gathered on the model had to be synchronous and the time relation of these data with the wind tunnel parameters had to be known.

3. Since the model had to fly essentially freely in the tunnel, any data transmission system could not perturb flight parameters.

4. The models flown in typical tunnels were usually less than 10 ft in length. Therefore, the instrumentation system had to be small, and its construction and form factor had to be conducive to simple installation, balance, and trim of the aircraft model.

By using modular construction, a system was built that was well suited for static and dynamic investigations in which a moderate number of relatively accurate channels having matched time and phase characteristics are required. Its physical features provided a flexible adaptation to various model configurations. Microelectronic techniques using integrated and hybrid thick-film circuits on alumina substrates were used in performing digital and analog functions that provided significant advantages to packaging a system in which accessibility, size, and weight were the pertinent constraints. The signal conditioner portion of the system is seen in figure 33, where the white plates are alumina substrates having printed conductors and resistors and attached discrete components. It was necessary to use hybrid construction because the wide temperature variations in the tunnel precluded the use of temperature sensitive integrated circuits in parts of the circuit. The system performance is summarized in table XXI.

A hybrid miniaturized power amplifier for a VHF transmitter was developed at Langley Research Center by J. J. Davis. The purpose of the project was to reduce size and weight without altering operational parameters. For this particular project, silicon-integrated circuitry was not practical due to parasitic capacitance and the unavailability of an integrated, small rf inductor. The hybrid technique using discrete components offered the most practical approach with better components performance and isolation. To determine the applicability of this technique, a 2.5-W hybrid VHF power amplifier was developed.
Problem areas in this circuit were selection of a rf coil sufficiently small and of adequate \( Q \), elimination of regenerative feedback, selection of transistor packaging, resistor and capacitor selection, and substrate packaging. An air core rf coil of \( \frac{1}{8} \)-in. internal diameter and \( Q \) of 140 was selected over a more efficient air coil of 3-in. internal diameter and \( Q \) of 190 for size considerations. Lower efficiency iron core solenoids of smaller size were unacceptable due to \( Q \)’s less than 100 and resulting inefficiency. It was found that careful circuit layout reduced regenerative feedback or oscillation due to coupling in the ground plane which is a common problem in high-frequency amplifier stages. Very small discrete components, such as resistors and capacitors, contributed to improved circuit performance. The reduction of lead
TABLE XXI.—System Performance Characteristics

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of channels</td>
<td>20 channels (simultaneously) or 120 channels time shared</td>
</tr>
<tr>
<td>Module capacity</td>
<td>5 channels</td>
</tr>
<tr>
<td>Typical weight and volume</td>
<td>113 g and 15.3 cm³/channel</td>
</tr>
<tr>
<td>Frequency response</td>
<td>0 to 200 Hz (0 to 1 kHz with increased noise level)</td>
</tr>
<tr>
<td>Channel time delay</td>
<td>2.1 MS ± 150 sec</td>
</tr>
<tr>
<td>Stability over an 8-hr period</td>
<td></td>
</tr>
<tr>
<td>a. Gain stability</td>
<td>1 percent or less</td>
</tr>
<tr>
<td>b. Zero stability</td>
<td>2 percent for 25°C delta</td>
</tr>
<tr>
<td>c. Linearity stability</td>
<td>0.2 percent or less</td>
</tr>
<tr>
<td>d. Noise level</td>
<td>0.2 percent or less</td>
</tr>
</tbody>
</table>

lengths on these components allowed flexibility of placement and reduced stray capacitances and inductances.

The TO-50 transistor package was selected in preference to the TO-5 and TO-18 for all stages except the final, for the following reasons:

1. Lower package profile height
2. Ribbon leads for reduction of lead inductance
3. Case directly solderable to a brass chassis for best heat sink conditions
4. Base, collector, and emitter leads electrically isolated from case for direct case heat sinking

The final power transistor was available in a small flat package, approximately 1/16 in. in height and 1/4 in. in diameter, which resulted in a volume reduction of 100 to 1 over a standard TO-60 case. The flat package had ribbon leads which enabled direct soldering to a brass plate for ideal heat transfer.

The required range of resistors, especially down to 18 Ω, discouraged the use of screened resistors, and screened capacitors of high-Q values were unavailable at the time of the designing. As a result, pellet resistors and capacitors were used. Alumina substrates proved more suitable than printed circuit boards for the following reasons:

1. The high thermal conductivity of alumina enabled the substrate to act as a heat sink for transistors and other discrete components.
2. The alumina substrate was more stable under repeated heating operations.
(3) Heating for reflow soldering attachment of components was done through the substrate as the high-density packing and small conductor pads did not permit application of heat from the top of the substrate.

The project established that a VHF transmitter may be developed using hybrid miniaturization fabrication techniques to reduce size and weight without significantly degrading operational characteristics. The final assembly is shown in figure 34.

In a project at the General Electric Co.'s Valley Forge Space Center, sponsored by the Jet Propulsion Laboratory, hybrid thick-film microcircuitry has increased the piece part density of space power conditioning equipment (ref. 207). In the past such equipment has not kept pace with improvements in other subsystems since the nonuniform sizes and the shapes of mechanical devices and electrical parts did not permit efficient packaging. Thin- and thick-film microcircuit techniques have been applied to power

Figure 34.—Hybrid microelectronic VHF power amplifier mounted on alumina substrates and capable of handling 2.5 W.
equipment, but the rate of application has been slow due to the small degree of standardization and problems with high thermal densities that occur when high-power parts are put into small volumes.

One task of the Thermoelectric Outer Planet Spacecraft (TOPS) project was to develop a hybrid microcircuit for the electronic parts of a dc-to-dc converter. The converter receives a relatively constant single-voltage dc supply and converts it into many different dc voltages of different power levels. A basic, multipurpose circuit was built that could be used to satisfy 35 separate requirements on the TOPS project with conditioned power levels from 1 to 25 W. Three models were identified for this range of power and all three could be built on the same conductor layout, with variations in the values of only seven parts.

Flat-pack materials and construction enhanced thermal conductivity and balanced the increased thermal density with higher thermal conductivity and shorter thermal paths. The alumina substrate supported the circuit elements and provided high electrical insulation and thermal conductivity to the bottom of the metal flat pack that was used. The flat pack in turn was bonded to a metal heat sink with a highly conductive paste or a low-temperature solder. The few efficient thermal interfaces provided excellent heat transfer. The flat pack was rated at 25 W/in² with adequate heat sinking.

A comparison of the flat-pack design to that of a discrete piece part circuit indicated volume and weight reductions of 80 percent. Interconnections to the remaining converter piece parts were decreased from 44 to 13. The smaller circuitry also decreased opportunity for noise coupling into adjacent circuitry. A picture of the thick-film portion of the circuit may be seen in figure 35.

The Guidance and Control Division, Manned Spacecraft Center, is working on a means to monitor more effectively the functioning of equipment in aircraft or spacecraft. The concept is to build small “microprocessor” units which will receive and process test signals in close proximity to the signal source. A highly refined signal is then sent back to a central monitoring station. Savings on wiring needs, increased reliability, and decreased size and weight of the monitoring system are expected. Maximum use of large-scale integration (LSI), implying over 100 circuit functions per chip, and IC technology is planned within a hybrid thick-film framework.

Requirements include a high packaging density and system partitioning flexibility. Design limitations also include a con-
servative, high-reliability approach that demands placing LSI chips in a hermetic package, less than 1 in. square. Interconnections for LSI chips that also served as structural members and/or as aids to heat transfer seemed a logical design concept.

The recent availability of ceramic multilayer wiring boards provided a solution to these requirements. The ceramic multi-
layer wiring board provided functions similar to one made of epoxy glass but with these advantages:

1. Higher thermal conductivity due to alumina construction
2. Ability to serve as a part of the hermetic package
3. Capability of smaller conductor paths and through holes

The 1-in.-square board can accommodate nine 140-mil-square LSI chips with 32-lead pads each. It has 72 input/output (I/O) pins around the periphery and a cover metallization stripe that runs between chip depressions and the I/O pins. Each board is capable of up to 10 layers of circuitry, with the internal wiring consisting of tungsten, platinum, or moly-manganese metallizing with sheet resistivity of about 0.01 Ω sq. A 1-in.-long conductor 10 mils wide would have a resistance of 1 Ω. The alumina layers between the wiring planes are typically 5 to 10 mils thick. The number of I/O pins and their geometry may be changed by going to a rectangular form factor and/or to a second row of I/O pins around the periphery. In this design the pins are swaged into metallized holes in the ceramic. After assembling the LSI circuits on a board, a hermetic package is formed by sealing the top and side walls in place over the metallization pattern.

Five multichip LSI packages are stacked and joined by oven soldering. The pins from one package are bonded to the next lower package in the stack. This forms a microprocessor module. Repairs can be made by removing a defective multichip LSI package and replacing it. Besides providing electrical I/O connections, the pins provide both mechanical integrity and heat-transfer paths vertically through the module.

![Diagram of a transistor](image)

**Figure 36.**—Schematic drawing of a field-effect transistor based on silk-screened CdS.
Thermal calculations show that the module can easily dissipate 5 W, assuming a 0.7-by 0.7-in. 50°C sink in good contact with the bottom LSI multichip package in the stack. The temperature differential between the center of the top multilayer LSI package and the heat sink was found to be 25°C.

The importance of this work lies in the design concept that minimizes size and weight and still stresses high reliability and flexibility in system partitioning. By using alumina multilayer substrates of good thermal conductivity and high structural strength, up to nine LSI chips can be put into one hermetically sealed package. The large electrical contact pins on the periphery of the packages enable joining by low-temperature soldering, which does not harm the LSI chips. They also enable disjoining for repair of the module. The pins contribute to the structural integrity of the module and provide thermal conduction paths to the heat sink.

New Film Preparation Techniques

Thick-film deposition techniques have been used for many years for preparing resistors, capacitors, and conductors, but not for active devices. Langley Research Center has sponsored studies on the properties of field-effect transistors made by thick-film screening techniques (refs. 208 and 209). Semiconducting CdS was deposited onto a substrate by silk screening, electrodes by vacuum deposition, and the gate insulator by either vacuum deposition or chemical vapor techniques.

A cross-sectional view of the thick-film field-effect transistor is shown in figure 36. Cadmium-sulfide ink is first applied to the substrate by conventional silk-screening techniques and fired in air at a temperature of 500°C. Source and drain electrodes are applied by evaporating aluminum through mechanical masks. Accurate spacing between the source and drain is achieved by using a 0.001- to 0.003-in. wire as the mask. Vacuum-deposited SiO or SiO_2 made by pyrolytically decomposing silane have been used for the formation of the gate insulators with no great change in properties.

Transconductance values of close to 1000 μmhos can be obtained with a channel width of 0.001 in. The channel length is also 0.001 in. Besides good saturation characteristics, the source-to-drain current can be as low as 1 μA.

Practical thick-film active devices, if available, would broaden the capability of hybrid circuits. Instead of using discrete transistors or integrated circuits, it would be possible to form the
active devices using economical thick-film processing, as for example, screen printing and nonvacuum processing. Instead of matching one's requirements to commercially available active devices, the needed properties could be designed directly into the circuit. The work on CdS thick-film active devices is a first step toward this development.

A new method to sputter ceramic insulators as well as other materials has been developed at Lewis Research Center (ref. 210). It combines the advantages of ion plating with the versatility of a radiofrequency-sputtered source and is described as rf sputtering with pulsed high-voltage (HV) dc. Its advantages compared to other film deposition methods may be seen in table XXII.

In the new technique, an rf-sputtered source is substituted for the normal thermal evaporation source used in ion plating. The one major disadvantage of ion plating, the use of a thermal evaporation source, is eliminated, and film materials other than just elemental metals of those compounds that do not dissociate before evaporation may be deposited. The key to the new technique involves a modification of the ion-plating process. In normal ion plating the thermal evaporation source provides rapid deposition. Ion bombardment causes only a slight loss of plating. However, in rf sputtering, the rate of film deposition is sufficiently slow that ion bombardment on the object to be plated removes the entire film. Therefore, the ion-plating process was modified to reduce the rate of removal of the new film due to ion impingement. The rate reduction was effected by pulsing the negative high dc voltage to the object to be plated. To do this, a third electrode was inserted between the sputtered source and the object to be plated. This electrode was a screen with a hole in the center.

A technique for epitaxial crystalline thin-film growth on cold substrates has been developed under NASA sponsorship by Physics Technology Laboratories, Inc. (ref. 211). In the past it was necessary to heat substrates to temperatures of 250°C or higher. The elevated temperature was needed to provide energy for molecular mobility and resulting crystal growth and orientation. In the new technique, molecules from a sputtered target are dislodged and accelerated to kinetic energies of 3 to 20 eV by impacting argon ions from a high-energy shaped ion beam. The higher energy provides the needed mobility and assists in the epitaxial growth on the substrate.

The pertinent features are shown in figure 37. A shaped argon ion beam of about 1 mA/cm² and energy up to 5 ke V is focused on-
| Line-of-sight deposition only | Yes | Yes | Yes | No | No |
| Plate complex shapes | Conditional\(^a\) | Conditional\(^a\) | Conditional\(^a\) | Yes | Yes |
| Plate with elemental metals | Yes | Yes | Yes | Yes | Yes |
| Plate with metal alloy systems | Some | Yes | Yes | Some | Yes |
| Plate with semiconductors | Some | Yes | Yes | Some | Yes |
| Plate with nonconductors | Some | No | Yes | Some | Yes |
| Film adhesion | Usually poor | Good | Good | Excellent | Excellent |

\(^a\) Must rotate object.

**TABLE XXII. Comparison of Pulsed High-Voltage dc, rf Sputtering With Other Film Methods**
to a target. Target material is ejected and collected on a substrate located outside the path of the ion beam. The substrate is unheated and at the ambient temperature of the vacuum chamber (approximately 75° C). One example cited is the deposition of a crystalline olivine (Mg$_2$SiO$_4$) target onto crystalline salt (NaCl). The deposition rate was 100 μm in 1 hr. The resulting film was shown to be crystalline in the isometric or hexagonal crystal system. Since olivine is orthorhombic, the evidence indicates that a new material was formed.

These last two techniques of film deposition are new tools that may be used in the study of thin films for microelectronic applications. Materials that portend useful devices if better properties can be realized are brought closer to practicality by such new approaches.

An investigation of refractory dielectric films for integrated circuits was sponsored by the NASA Electronic Research Center at IBM (ref. 212). The purpose was to —

1) Survey and analyze the literature to determine the most promising material superior to silicon dioxide that would serve as a dielectric and passivating film for integrated circuits.

2) Develop an insulator with a high softening point not reactive with semiconductor material at temperatures up to 1300° C. The insulator had to —
CERAMICS AND GLASSES IN MICROCIRCUITRY

(a) Form as good a dielectric as silicon dioxide in making metal dielectric-semiconductor capacitors,
(b) Mask against diffusion of n-type and p-type impurities, and
(c) Provide a passivating surface for integrated circuits.

(3) Design and build an integrated circuit based upon the results of work under item (2).

Silicon nitride was selected as the insulating material to be developed. The program included the investigation of growth, quality, diffusion masking, and integrated-circuit application. Growth studies covered nucleation, growth kinetics and alternate silicon nitride and silicon dioxide layer growth. Electrical measurements, chemical composition analysis, and chemical etch studies aided quality evaluation. The study included photoetch development as well as the investigation of the masking against dopant diffusion. Finally, the integrated circuit applications of silicon nitride films were pursued. A summary of the properties of SiO₂, Si₃N₄, and Si-Oₓ-Nᵥ films is given in table XXIII.

### TABLE XXIII.—Summary of the Physical Properties of SiO₂, Si₃N₄, and Si-Oₓ-Nᵥ

<table>
<thead>
<tr>
<th>Structure</th>
<th>SiO₂</th>
<th>Si₃N₄</th>
<th>Si₃N₄</th>
<th>Si = Oₓ = Nᵥ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point (°C)</td>
<td>1600</td>
<td>1900</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density (g cm⁻³)</td>
<td>2.2</td>
<td>3.4</td>
<td>3.1</td>
<td></td>
</tr>
<tr>
<td>Index of refraction</td>
<td>1.46</td>
<td>2.1</td>
<td>2.05</td>
<td>1.60–1.88</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>3.8–3.9</td>
<td>9.4</td>
<td>7.5</td>
<td>4.77–6.12</td>
</tr>
<tr>
<td>Dielectric strength (V cm⁻¹)</td>
<td>5×10⁶</td>
<td>1×10⁷</td>
<td>5×10⁶</td>
<td></td>
</tr>
<tr>
<td>Infrared absorption band (μm)</td>
<td>9.3</td>
<td>10.6</td>
<td>11.5–12.0</td>
<td>9.3 and 12.0</td>
</tr>
<tr>
<td>Energy gap (eV)</td>
<td>8</td>
<td>3.9–4.0</td>
<td>5.0</td>
<td></td>
</tr>
<tr>
<td>Thermal expansion coefficient (°C⁻¹)</td>
<td>5.6×10⁻⁷</td>
<td>3.0–3.5×10⁻⁴</td>
<td>5.0</td>
<td></td>
</tr>
<tr>
<td>Thermal conductivity (cal cm⁻¹ sec⁻¹ °C⁻¹)</td>
<td>0.0032</td>
<td>0.067</td>
<td></td>
<td></td>
</tr>
<tr>
<td>dc resistivity (Ω-cm) at:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25°C</td>
<td>10¹⁴–10¹⁵</td>
<td>10¹⁵</td>
<td>~10¹⁴</td>
<td></td>
</tr>
<tr>
<td>250°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>300°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>500°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Etch rate in 10:1 NH₄ F:HF (Å/min)</td>
<td>1000</td>
<td>&lt;0.1</td>
<td>5–10</td>
<td>33–400</td>
</tr>
</tbody>
</table>
Some values in the summary were from the literature, while others were results of the investigation.

Methods of preparing silicon nitride by the reaction of silane and ammonia were extended to include nitrogen, helium, and hydrogen as carrier gases. Films grown in nitrogen were superior to those grown in hydrogen or argon. The growth of silicon oxynitride was also investigated and these films had masking properties for high-temperature steam oxidation. MNOS samples had reasonably low flat band charge density and excellent high-temperature and room-temperature stability. Integrated circuits and diodes were passivated with silicon nitride and little effect was found with deliberate sodium chloride contamination after they were stressed 666 hr at 175° C.

**Information Transfer**

The complexity and variety encountered in microelectronic technology requires precise controls to produce high-reliability state-of-the-art circuits. The Hybrid Microelectronics Research Section, Astronics Laboratory, Marshall Space Flight Center (MSFC), has established procedures and controls and a MSFC laboratory document describes specific processes and procedures to establish adequate controls and quality inspection criteria for fabricating microelectronic circuits (ref. 213). As the technology and equipment are advanced by laboratory experience, the document is updated and expanded. The Laboratory tests and evaluates components used in hybrid microcircuits. This enables MSFC to determine if these products are of suitable quality for NASA applications. The passing or failure of tests gives a valuable benchmark with which to evaluate products. In addition, prototype hybrid microcircuits are designed, fabricated, and given engineering evaluation in the MSFC laboratory.

A microelectronic device data handbook has been prepared for NASA by ARINC Research Corp. (ref. 214). The two-volume handbook compiles many reports of research, development, and application efforts. The handbook is written so that a minimum of advanced theory and mathematics is needed to use it.

The first volume discusses a variety of subjects related to integrated circuits. These subjects include physical description, costs, development trends, basic production processes, and integrated circuit design. Criteria important in systems design are covered, as are packaging, logic systems, redundancy, maintainability, testing, quality assurance procedures, specifications, procurement standards, reliability, and physics of failure.
The second volume lists manufacturers, a catalog of microelectronic devices, and a collection of schematic drawings of available circuits. The handbook provides general information on the technology of integrated circuits and is not intended to supply solutions to specific design problems. It is a good source of reference for an overall view of microelectronics device data.

A general description of the contributions of NASA to the microelectronics field was made in the technology utilization survey Microelectronics in Space Research (ref. 215). This document reviews the field of microelectronics in four main categories: (1) technology and techniques, (2) device design and development, (3) reliability, and (4) applications.
Technology Transfer to Nonaerospace Uses

NASA efforts in electronics have centered on the need for small, lightweight systems. High reliability was needed to provide safety for astronauts and aviators and to prevent failure of extremely costly spacecraft and high-performance aircraft.

The importance of electronics to NASA efforts has been primarily in controls and communication. Control of spacecraft navigation and satellite positioning and altitude is based on electronic sensors, circuits, and computers controlling propulsion. The importance of communications was brought to the attention of the entire world by the television record of man's first visits to the Moon and the suspense-filled moments during the communications blackout of spacecraft reentering the Earth's atmosphere.

The success of the lunar program was paralleled in the development of supporting technology. The use of ceramics in electronics has been expanded during this period and in this chapter electronic systems using these materials will be cited with examples of how they have or may be of value in commercial and consumer-oriented applications. Future developments in ceramics for microelectronics will also be discussed.

DESIGNING CERAMICS INTO MICROCIRCUITRY

In designing ceramics into microelectronics systems, a dismaying number of variables must be considered and compromises accepted. For example, design of the package requires consideration of the following variables (ref. 217):

1. Electrical (noise, speed, crosstalk, etc.)
2. Thermal dissipation (cooling available, ambient temperature, component capability, etc.)
3. Size (weight, volume, shape)
4. Environment (vibration, shock, temperature, humidity, etc.)
5. Reliability (components, process, system, etc.)
6. Maintainability (field conditions, logistics, etc.)
(7) Repairability (in the field, throwaway, etc.)
(8) Interfaces (mechanical, electrical)
(9) Cost (labor, material, testing, etc.)
(10) Schedules (component availability, design, drafting, manufacturing capability, etc.)
(11) Customer preferences (experience, specifications, etc.)
(12) Producibility (automation, in-house know-how, etc.)

These factors are complex, interdependent, and difficult in some cases to describe in numerical terms. Arriving at an overall figure of merit is not possible. Yet attempts are being made to select packaging technology and design by taking into account the tradeoffs which must be accepted.

The designer first compiles the functional requirements for the package:

(1) Support for chips and films
(2) Interconnections
(3) Power distribution
(4) Cooling path
(5) Mechanical protection
(6) Environmental protection
(7) Leads for inputs, outputs, and power

Tradeoffs are related to the application and technology restraints. For meaningful dialog and collaboration between designers and materials and processes technologists, design criteria have to be translated into terms of technology constraints. On these must be superimposed the product goals in cost, performance, and reliability (ref. 218).

Similar considerations and communications problems arise in the design of every function in the microelectronic system, including the ceramic-based components. The decision factors start with the technical feasibility of performing the required functions within the economic constraints. Tradeoffs involve whether to go the route of integrated circuits, thick films, thin films, or hybrids; whether to use a film or a discrete chip, and what interconnection methods are feasible.

Special requirements may dictate a specific technology. Thus, if the circuit is to be operated up to 125° C, the requirements of high thermal dissipation preclude organic components and ceramics become the dielectrics of choice. If very low aging rate of resistors is paramount, thin-film technology may be obligatory. If small size and low weight are prime considerations, monolithic integrated circuits may be the only feasible approach.

The following sections will describe opportunities which ce-
ramics offer the designer in terms of electrical properties, thermal dissipation, environmental considerations, reliability, and design flexibility, using examples derived from NASA experience.

**Electrical Properties**

Ceramics are versatile in their electrical properties and a wide range of values is available. The dielectric constant can vary widely from 3.8 for glassy silica to nearly 10,000 for ferroelectric ceramics. Electrical resistivity can range from greater than $10^{14}$ \( \Omega \cdot \text{cm} \) for many insulators to about $1 \times 10^{-5}$ \( \Omega \cdot \text{cm} \) for thick-film conductors. Provision of intermediate levels of properties makes ceramics especially useful to the electronic designer.

An example of properties that have been extended with the necessary control is seen in the development of thick-film capacitors at Langley Research Center. Initial efforts produced films in the Laboratory with dielectric constants of about 100, but today dielectric constants may be as much as 2000. Thick-film capacitors deposited onto substrates are being applied in circuitry for moderate capacitance. Their disadvantages lie in limited capacitance and the use of considerable substrate area. Similarly, early thick-film resistor formulations had sheet resistivities up to about 20,000 \( \Omega / \text{sq} \), but today values up to 20 million \( \Omega / \text{sq} \) are possible. Both of these developments have occurred while still retaining the ability to form and apply the films in circuitry as needed. Since thick-film technology is still rapidly evolving, the studies on reliability of thick-film components sponsored by NASA (see ch. 3) should aid all industry in determining capabilities of the technology.

**Thermal Dissipation**

An important problem in microelectronics is the removal of heat from components; as circuitry gets smaller and smaller, this problem becomes more critical. The trend in thermal dissipation requirements for circuitry is shown in figure 38 (ref. 218), and it appears that this problem will require more attention in the future. The high thermal conductivity of certain ceramics is an advantage when they are used for substrates or packaging. A source of 0.10-in.-diameter on a 0.060-in.-thick substrate will increase in temperature 1 \( ^\circ \text{C} \) per watt of power if the substrate is beryllia; 8 \( ^\circ \text{C} \) if alumina; 117 \( ^\circ \text{C} \) if glass; and 1000 \( ^\circ \text{C} \) if an organic. Of course, the deterioration or failure of circuit elements (or substrates) would occur before these highest temperature differentials would be reached.
The good thermal conductivity of alumina ceramics was one of the reasons for its use in the high component density "microprocessor" designed by Manned Spacecraft Center personnel and constructed by the MIT Instrumentation Laboratory. An alumina substrate also was used in the thick-film microcircuitry developed for power conditioning equipment in the TOPS program. The safe power dissipation for this design was 25 W/in$^2$ of substrate. (Both of these NASA developments were described in ch. 5.)

Commercial applications of ceramics include substrates and packaging where high concentrations of heat must be dissipated. One example is in computers where manufacturers are using alumina and beryllia ceramics.

Future circuitry requirements for thermal dissipation may not be satisfied by single-phase ceramic materials; "composite-ceramics" may be needed. Significant work is being done in composite ceramic structures for applications other than microelectronics, and this may be transferred to substrate technology.
For instance, ceramic composites for structural and thermal protection have been designed as laminates, dispersed fibers, and other oriented two-phase components. An oriented, second phase of extremely high thermal diffusivity or of internal “heat pipes” could serve as heat transmitting channels.

**Environmental Considerations**

The high-temperature capabilities of ceramics suggest applications of microelectronic circuits in systems previously not possible. Besides their use in NASA systems, where stringent environmental conditions must be satisfied, ceramic systems have been used commercially. As an example, a recent paper (ref. 219) describes a voltage regulator based on thick-film technology designed to be mounted in an automobile generator housing where temperatures up to 125° C are encountered. Previously, an electromechanical type of regulator mounted on the automobile firewall could not withstand these temperatures and meet other requirements.

The design selected was a thick-film hybrid integrated circuit with alumina substrates, since this best satisfied electrical and environmental requirements. High transient voltages (100 V) and high temperatures (125° C) in the generator housing where the regulator was to be mounted precluded the use of completely monolithic structures. Components included a high-current transistor and diode, monolithic integrated circuit chips, and thick-film networks using conductive, resistive, and thermistor compositions. Input and output sections on separate alumina substrates were fabricated and tested prior to final assembly to maximize production output and minimize circuit rejects.

This particular design has been cited to illustrate a specific use, and how hybrid circuitry based on ceramic technology satisfied the needs. Microcircuitry for control purposes in clothes dryers, washing machines, dishwashers, ovens, range tops, and furnaces are suggested by the high-temperature capabilities of the ceramic-based hybrid technology.

The tolerance to adverse environments of ceramics could be useful not only in consumer applications, where high temperatures may be encountered, but also in industrial processing where high temperatures and harsh conditions are inherent. For example, ceramic substrates are used in chemical-vapor deposition. In this type of processing, the substrate at elevated temperature is subjected to highly reactive vapors during film deposition. The high-temperature tolerance and chemical inertness of ceramics
also permits better cleaning and bakeout, while their low vapor pressure permits their inclusion in high-vacuum equipment.

Reliability

Circuit deterioration can occur when components are used that lack stability with time, changing atmospheres, and/or elevated temperatures. When many components are utilized, the likelihood of circuit failure is very high. One approach to this problem is to design in redundancy. This technique is common in integrated circuits, since individual components and circuits are low in cost. Another approach developed to a high degree of perfection at Marshall Space Flight Center involves study of accelerated aging at elevated temperatures to predict component behavior. Thick-film circuitry and discrete ceramic components may be constructed with high reliability because of the stability or predictable behavior of ceramics with changing conditions. One reason is that ceramic-based circuits and components are processed at high temperatures and are thereby stabilized when used at or somewhat above room temperature. Auto manufacturers are now producing hybrid thick-film circuitry for automobile radios and antiskid devices. A major reason for using this type of circuitry is its demonstrated reliability.

The reliability achievable in integrated and hybrid circuitry indicates that future television sets and other electronic equipment could be virtually failure free. The reliability technology established in NASA programs will also aid design and performance in other fields.

Design Flexibility

One advantage of ceramic thick-film hybrid microcircuitry is the flexibility in design that is possible (ref. 220). A design may include mixed monolithic integrated circuits and other individual active or passive components. The passive components can then be trimmed to precise tolerances. For evaluation, such a circuit can be breadboard constructed in-house. Results very close to production circuits can be achieved, and the transition from development to production is relatively simple. A further advantage is the retention of proprietary features of circuits by keeping all design in-house.

Most of the circuits described in chapter 5 were constructed at least partially of thick films to have design flexibility and meet the requirements. The microelectronic instrumentation system for scaled aircraft constructed by Langley Research Center utilized thick-film technology for the signal-conditioner portion of the
circuit. Wide temperature variations in the wind tunnel prevented the use of temperature-sensitive integrated circuits. By using thick films, the necessary system performance was maintained and size and weight reduced.

The miniaturized power amplifier for a VHF transmitter (ch. 5) was also constructed of thick films. The use of IC's was not possible due to parasitic capacitance and the unavailability of an integrated, small rf inductor. For this particular design, small discrete components with thick-film interconnections of an alumina substrate provided adequate size and weight reduction.

Hybrid thick-film facilities are becoming routine for nearly all industries producing electronic products.

**TRENDS IN CERAMICS FOR DEVICES**

The use of ceramics in microelectronics will expand in the future because the properties of ceramics will be essential for many applications. In addition to new compositions, purer materials and greater control of microstructure and properties will be demanded. In applications where one material cannot provide all of the desired properties, composite materials will be more widely utilized. The materials science and engineering concept will pay off more and more in selection and invention of the best blend of materials to meet design requirements.

It is expected that the impetus toward higher circuit density, improved conductor transmission properties, lower voltage drops in conductors, and increased thermal dissipation in substrates will be met by lead reduction, lower dielectric constants, improved conductor geometries, higher lead electrical conductivity, and higher thermal conductivities.

Requirements such as these may bring development of "structured substrates" in which various portions will have different properties as do different portions of an integrated circuit chip. For example, at microwave frequencies an efficient waveguide requires a high dielectric constant and low-loss dielectric materials. An active device adjacent to the waveguide might require a high thermal conductivity mounting. Today it is not possible to get this combination of properties in one substrate material. In the future, perhaps, a substrate having good thermal conduction properties and good waveguide properties in designated areas will be developed.

Multilayered substrates and layered conductors, crossovers, and capacitors are examples of the trends. Another is the use of selected glazed areas for thin-film capacitors on substrates to have
sufficient surface smoothness, while using unglazed areas for mounting heat-generating components. The development by Lewis Research Center of a thermionic seal that displays both good thermal conductivity and high insulation resistance is one such contribution.

Capacitor developments have been based on thin, flaw-free dielectric layers. It has long been recognized that the intrinsic properties of the ceramic dielectrics far exceed ability to form sufficiently high-quality layers. Plasma- and flame-spraying techniques were developed at Langley Research Center to deposit these films as glasses convertible to crystallized ceramics. The ability to form thin dielectric layers by casting or doctor blading has given rise to the multilayer capacitor industry with its high-capacity chip capacitor. These product advances are ascribable to better quality chemicals than were available previously and knowledge of how to use plastics technology to form films. Further advances may be possible.

Additional novel processing capabilities will provide opportunities for innovations in components and circuitry. NASA- and AEC-sponsored work in characterizing ceramics, such as BaTiO₃, from particulates to finished ceramics has provided information that lays a basis for advances. The multilayer glass-ceramic capacitor resulted from advances by the glass industry. The recognition of the potential of a process for high dielectric constant glass ceramics led to the systematic development of this class of materials. This development was then extended to thick films where glass-film capacitors had been limited by low dielectric constant. Today thick-film capacitors are available in reasonably high dielectric constants (up to 1000) using the glass-ceramic concept. Other components are being improved by this approach.

A limit in properties has not been reached. As a safety factor in case of flaws, capacitor films and multilayers are made many times thicker than their intrinsic dielectric strength requires. More uniform microstructures are still possible for the high-dielectric constant ceramics, leading to more uniform capacitances, less sensitive to temperature variations and aging. Also, advances in designs and configurations are still to be expected with the discovery and development of new manufacturing processes. In the future we can expect to see evolution similar to that we have seen in the past—purer chemicals affording better property control and improved properties, which in turn may justify new manufacturing technology. The reliability and cost savings in
microelectronics should create opportunities for new products and technologies. These in turn could justify developments in all components, circuitry, and systems.

Resistor technology is an integral part of the materials and processes advances necessitated by microelectronics technology. The limitations of carbon composition and wirewound resistors led to film types of discrete resistors with improvements in reliability, stability, and reproducibility. In film technology, resistive networks on a single substrate have further improved reliability, tracking, and costs. Initial impetus for the new technology was provided by military and space requirements, but now civilian needs require further advances.

Continued improvement of resistors will call for great effort in microcircuitry film technology. Improvements in temperature coefficient of resistance, noise level, voltage coefficient of resistance, etc., will continue to be made both from materials and processing developments.

One development in thick-film technology has been preparation of the resistor material in a flexible cast film for commercial applications in order to eliminate difficulties in the screen-printing process. This approach is an attempt to reduce waste and labor, improve control of resistance, shorten design leadtimes, and increase the user's control over the circuit design. Work is also proceeding to develop interface capability between the various microcircuitry technologies; e.g., by developing high-value resistor technology compatible with thin-film integrated circuits (ref. 221). Resistive cermet films of about 2- to 3-μm thickness have been deposited on a number of common substrates including alumina, glazed alumina, silica-passivated silicon, and high-resistivity glass by screen printing. These can then be selectively etched using photoresist techniques. With such processing it has been possible to achieve resistivities as high as 100 kΩ per square, suggesting suitability in applications requiring semi-precision resistors on monolithic silicon chips.

Whatever the future holds, materials will be a key to progress. Improved materials will be necessary to build more efficient devices, and ever-improving materials will be appearing for a wider range of applications.

THE PROCESS OF TECHNOLOGY TRANSFER

A wide range of thick- and thin-film components and circuitry is now used not only on NASA and DOD space missions, but also increasingly in commercial, consumer-oriented applications. Es-
especially pertinent to this survey is the development of technologies within the space community, and their subsequent use in consumer and industrial products and processes.

To illustrate what has happened, consider the work done at Langley Research Center, in-house and on contractual assignments, in thick-film microelectronics. This work was begun because of NASA's need for highly reliable miniature components for flight and instrumentation projects. Figure 39 shows how, beginning in 1963, materials-oriented work on resistor pastes, conductors, and crossovers, laminated dielectrics, and thick-film capacitor materials led to the establishment of an advanced process technology laboratory. Continued work in parallel to work at NASA and in the electronics industry on active devices led to the widespread use of hybrid circuitry by 1967. The maturing of hybrid technology is verified by the holding of the First Technical Thick Film Symposium in 1967, followed by the founding of the International Society for Hybrid Microelectronics. These hybrid circuits have been used by NASA on systems such as C5A telemetry, the NASA recovery beacon, airplane pulse-code-modulated (PCM) clock and analog/digital converter techniques for helicopter blade studies.

R. L. Stermer, Langley Research Center, reported that the telemetry developed for the C5A is being applied to commercial aircraft. The recovery-beacon circuitry has potential use for tracking automobiles on highways and possibly for monitoring private-airplane crashes in remote areas. The "fallout" from the work done for the airplane pulse-code-modulated clock could occur in commercial time-sequence machines for banks, offices, and factories. The helicopter blade studies conducted by NASA used compact, lighter analog/digital converters which could supplement present-day commercial devices. These are convincing illustrations of how microelectronic circuits using ceramic materials for space applications can result in useful consumer/commercial applications.

Hybrid integrated circuits have appeared in many consumer-oriented applications. With the advent of new and cost-lowering production techniques, microelectronic circuits by the billions should appear on the market. It is becoming apparent that microelectronics, and especially its hybrid approach, is both being adopted in every type of electronic product line, and making feasible entirely new applications.

In NASA-sponsored work materials-devices-circuits-systems interfaces were established with considerable interaction of
Figure 39.—Development and technology interactions in microelectronics thick-film work at Langley Research Center. (This chart was supplied by C. M. Husson, Langley Research Center.)
various disciplines such as materials science, solid-state physics, and electronic engineering. NASA seeding developed a confidence level which, in turn, accelerated commercial development of hybrid circuitry. The industry's continued involvement with this technology can be seen from the bibliography. In spite of the rise in use of integrated circuits and their built-in components, miniaturized chip components and film circuitry often satisfy total circuitry requirements.

MICROELECTRONICS IN NONAEROSPACE APPLICATIONS

Inevitably the advances in materials, devices, and circuitry propagated by the special requirements of aerospace work are beginning to affect civilian activities. Hybrid microcircuits are already being designed into automobiles, appliances, hearing aids and other medical equipment, radio and television, telephones, and in many other modifications of established products. No one has a crystal ball prescient enough to predict completely the consumer products which the advantages of hybrid microcircuitry will inspire. In many applications, even the imaginations of science-fiction writers may be outstripped.

A cursory listing of known products includes applications to such major industries as computers, communications, entertainment, toys, appliances, transportation, industrial controls and instrumentation, and medical electronics and biotelemetry.

The first major impact of the new microcircuitry on our society was in high-speed computers. IBM has taken advantage of the space savings, cost savings, and reliability which contribute minimum downtime and maintenance to computer equipment. Thick-film and hybrid circuitry went into mass production more rapidly than medium- or large-scale integrated circuitry, cryogenic or room temperature thin films, or other alternatives.

As a consequence of the stimulation of the supply of alumina substrates, resistive and conductive pastes, sealants, and other materials for hybrid circuitry, manufacturers of computers and calculators in the whole range of sizes and markets have followed the hybrid microcircuit route. Much of this work is now in the developmental stage and soon the consumer will profit in terms of lower cost and more reliable and versatile computation.

Competitive computer manufacturers have not been the only beneficiaries from this scaled-up demand for microelectronics. Many small- and medium-sized supplier companies have been started or revitalized by the rapidly growing demand for materials, components, modules, and subassemblies. Their facil-
Ities, skills, and products will inevitably feed into other consumer and industrial devices. In addition to large computer systems, ceramic substrate circuitry has been used in small desktop calculators, minicomputers, cash registers, and other business machines.

The American Telephone & Telegraph system has been another potent nucleator of new products derived from microelectronics. Its demands for quantities and surface finishes for alumina substrates have been at such high levels that it has moved to establish its own pilot plant. Traditionally, Bell Telephone has made available any inventions resulting from its research and development through a licensing program. The setting up of a pilot plant pushes progress in its suppliers and licensees and establishes a control over costs. The goal is an economical substrate meeting a surface-finish requirement of 5-μin. peak-to-valley for interconnections, and 1 μin. for tantalum thin-film capacitors (refs. 222 to 224).

A significant nonaerospace application of microelectronics in telecommunications is the use of ceramic substrate circuits in a new tone generator for telephones. Miniaturization and cost reductions were obtained in designing the tone generator by using thin films and beam-leaded integrated circuits (ref. 223).

The passive network which controls the Touch-Tone calling frequencies consists of tantalum thin-film resistors and capacitors, deposited on separate substrates and interconnected with gold tape leads. The oscillator frequency was made insensitive to temperature changes by using resistors of tantalum containing a controlled amount of oxygen, instead of titanium nitride, so as to obtain a TCR equal in magnitude but opposite in sign to that of the thin-film tantalum capacitor. In 1969, 0.8 acre (4.7 million in²) of flat ceramic sheet was used by the Bell System for this technology. By 1974 the use will increase by a factor of 16 to 13 acres of ceramic sheets (ref. 224).

Ceramic-based microcircuitry has also found use in more complex telephone systems such as Bell's Digital Transmission System, now being developed for medium-speed toll transmission. It uses monolithic circuits in the digital part and thin-film resistors in the coder and decoder units. The use of these thin-film resistors provides high precision which would have been very expensive with conventional resistors. The resistors, on the other hand, can maintain voltages independent of temperature. The knowledge gained in this transmission system is being applied by AT&T to the design of future, higher speed systems.
Another nonaerospace application of tantalum thin-film passive components by Bell Laboratories is in microwave circuitry. Such circuits are used in high-grade telephone radio-relay repeaters, with significant improvements in reliability and equipment uniformity. Such microwave integrated circuitry (MIC) is also being used for advanced radar systems in monitoring commercial as well as private airplane flights.

In addition to ceramics as substrates, the telephone companies are interested in their use in packaging. Important as the packaging is for high reliability, the fact that the package costs more than the chip which does the vital work is a limitation on the extent to which microelectronics can supersede existing art (ref. 224). One approach to lower packaging costs has been thin layers of insulators over the critical junction regions which have been described under “Crossovers and Passivation” (ch. 5). Again, lowered costs will predictably open new and expanded markets.

Other consumer-oriented industries also have been investing heavily in automating integrated circuit manufacture with the objective of lowering costs. Aside from a vast, hardly scratched market in color and monochrome TV, phonographs, radio receivers, tape players, and other entertainment end uses, wide use is foreseen in washers, dryers, air conditioners, automobiles, mixers, and other products. Other uses projected for low-cost integrated circuits include radio transmission; AM and FM circuitry; and UHF television tuners; as well as other information, computation, and communication components for household use (ref. 225).

By 1980, it is predicted that the combination of microelectronics, computers, and software will tie many homes into vast information networks (ref. 226). Through them entertainment will become only one function of electronics in the home. Goods and groceries will be ordered and stocked, bills will be paid, educational information will be retrieved, opinions expressed, and other services made feasible.

A consequence of the burgeoning markets for the new components is the entry of established firms into product lines which are entirely novel for them. For example, Du Pont is to market a multilayer ceramic wiring system, designed for high-density packing and interconnection of multichip hybrid large-scale integration arrays (ref. 227). This is a major step from being a supplier of starting and semifinished materials toward providing a finished product.
Another example of how improved ceramic-based components for microcircuitry affects consumer products can be taken from the trends in the capacitor-chip markets. The industry’s chip production is expected to jump from 150 million units in 1969 to 400 million in 1970 (ref. 228). A major market is in automobile radios, but as costs continue to go down, it is believed that other new markets will be opened such as toys, personalized radios, and heart systems. Other markets envisioned are entertainment, commercial calculators, and automatic beacons for aircraft. In automobiles the reliability and stability of the cermet resistors has made them attractive for car radios as well as other applications such as generators, ignition systems, and instruments (refs. 219 and 229).

Hybrid thick-film circuits are also being utilized for solid-state electric power and control circuits. Glass-passivated power pellets and integrated control chips are being developed for high-frequency (25 kHz) lighting and induction heating. Advantages in cost, reliability, size, weight, and efficiency are anticipated. It is expected that this technology will have a major impact on the lighting industry, as well as on other electrical consumer products and services.

Thick-film hybrid circuitry is also being used in “optohybrids,” which act as sensors for light-emitting diodes. These are used in card readers for computer software, and may appear in many other extraordinary consumer products (ref. 230).

NASA has achieved major technological advances in space telemetry. Measurement at a remote location, and reproduction of the measurement at some other easily accessible location in a suitable form, has been greatly enhanced by the development of reliable microcircuitry. A lesser known but a very significant nonaerospace use of NASA-developed microelectronic technology has been in the remote monitoring of important biological functions and information—biotelemetry. New biotelemetry systems are being used in surgical and anesthesiological monitoring systems, in psychophysiology, and other medical procedures (ref. 231). Invariably, the advances in these consumer-oriented telemetry systems have been based on microelectronic circuits, such as ceramic-based integrated circuitry using transistors. Their adoption in medical electronics has brought about innovations in surgical and diagnostic procedures.

Advanced telemetry systems are also used in chemical plants, petroleum refineries, and paper mills for monitoring and controlling complex processes with obvious economic benefits.
Thus we have seen how microelectronic circuitry developed initially for space has been successfully diffused into nonaerospace applications. From a socioeconomic point of view, the most impressive factor is the breadth and diversity of these applications. They are already bringing about profound changes in the way people interact on their jobs, in education, in leisure activities, and in politics.

In retrospect, we can say that because of microelectronics—which ceramic components are an integral part—we have seen in recent years the accelerated development and application of newer and more efficient systems for industrial and consumer applications. In microelectronic systems, reliability and space-saving characteristics hitherto unattained in bulk devices are available, thus permitting nonaerospace innovations of significant socioeconomic value.
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Essentially the bibliography starts with 1963 as a year in which intensive activity in film and hybrid circuitry became evident through NASA involvement and widespread publications and symposia. A few earlier references which have historical interest are included. As with any bibliography in a rapidly moving field, the decisions on what to leave out were purely arbitrary.

Prime sources of current and advanced technology include the Journal of the American Ceramic Society, the IEEE Proceedings of the Electronic Components Conference, and the symposia publications of the International Society for Hybrid Microelectronics. Many of the papers in these publications list extensive bibliographies.


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Glossary

Active component: An electrical element capable of modifying an input voltage in such a way as to achieve rectification, amplification, or switching action; e.g., tubes, transistors, relays, etc.

Alkaline earth porcelain: A ceramic material composed principally of the aluminosilicates of calcium, strontium, or barium, usually with excess of alumina or silica.

Attenuator: A resistive network for reducing the amplitude of a signal without distortion of phase or frequency.

Beam leads: A generic term describing a system in which flat metallic leads extend from the edges of a chip component much as wooden beams extend from a roof overhang. These are then used to interconnect the component to film circuitry.

Bump: A small rise of metal formed on the conductors of a component chip or the pads of a substrate, to provide intercomponent connection (bump contact).

Capacitance: A measure of the amount of charge which a device can store in the dielectric between two conductors at a given voltage. The basic unit is the farad, but the smaller microfarad \((10^{-6} \text{ F})\) and picofarad \((10^{-12} \text{ F})\) are commonly used.

Charge carrier: A mobile conduction electron or hole in a semiconductor.

Chip: A single substrate on which all the active and passive circuit elements have been fabricated using one or all of the semiconductor techniques of diffusion, passivation, masking, photoresist, and epitaxial growth. A chip is not ready for use until packaged and provided with external connectors. The term is also applied to discrete capacitors and resistors which are small enough to be bonded to substrates by hybrid techniques.

Conductivity: The ability of a material to transport electrons, expressed as mhos, reciprocal ohms.

Corona: A discharge, or arc-over, at the edges of a dielectric due to ionization of the ambient atmosphere by high voltage.

Crosstalk: Interference picked up in an electronic circuit having its origin in a nearby circuit with which it is not connected.

Curie temperature: The temperature above which a ferromagnetic material becomes substantially nonmagnetic or analogously a ferroelectric material becomes nonferroelectric.

Delay line: A device used to slow down the transmission of a signal, in order that its use in another part of the system may be delayed. A common method is transducing the signal into an ultrasonic wave and back again.

Dielectric: A material with very low electrical conductivity (an insulator) when used between the plates of a capacitor; e.g., vacuum, air, mica, paper, polymer, porcelain, etc.
Dielectric constant: The ratio of the capacitance of a capacitor made with the given dielectric to that of the same capacitor having a vacuum as the dielectric. Also called permittivity and specific inductive capacity.

Dielectric strength: The maximum voltage gradient that a material can withstand without puncture or rupture, usually specified in volts per mil (thousandth of an inch) or volts per millimeter.

Discrete: Having an individual identity. Fabricated prior to installation, and/or separately packaged, not part of an integrated circuit.

Dissipation factor (D): The ratio between the loss current and the capacitive current of a dielectric. The reciprocal of the storage (or quality) factor (Q).

Epitaxial: Pertaining to a single-crystal layer on a crystalline substrate, and having the same crystalline orientation as the substrate; e.g., silicon atoms condensed from vapor phase onto a silicon-wafer substrate.

Filter: A selective network which will allow the desired frequencies to pass while suppressing or attenuating other frequencies.

Flip-chip: A generic term describing a semiconductor device having all terminations on one side in the form of bump contacts. After the surface of the chip has been passivated or otherwise treated, it is flipped over for attaching to a matching substrate.

Heat sink: A device for dissipating heat away from a component or assembly by absorption or conduction.

Hole: A mobile vacancy or electron deficiency in the valence structure of a semiconductor. It is equivalent to a positive charge.

Hybrid circuit: A combination of circuits in which basically different elements are used together (e.g., thick- or thin-film circuitry of conductors and resistors, with discrete integrated circuits, transistors, capacitors, etc., as components).

Integrated circuit (IC): An interconnected array of active and passive elements, inseparably associated on or within a continuous substrate.

Large-scale integration (LSI): Usually denotes arrays of integrated circuits on a single substrate that comprise 100 or more individual active circuit functions. The density of components range from 50 000 to 100 000 in-2.

Linear: Having an output which varies in direct proportion to the input.

Loss: (1) Energy dissipated without performing useful work. (2) A decrease in power suffered by a signal as it is transmitted from one point to another—transmission loss.

Loss factor: The characteristic (tan δ × dielectric constant) which determines the rate at which power is dissipated (and heat generated) in a dielectric material. It usually increases with increased frequency.

Lossiness: Power dissipation as applied to dielectrics.

Memory device: A device into which data can be inserted, retained, and retrieved.

Micromodule: A microcircuit constructed of a number of components (e.g., microwafers) and encapsulated to form a block that is still only a fraction of an inch in any dimension.

Minority carrier: The less-predominant carrier in a semiconductor. Electrons are the minority in p-type; holes are the minority in n-type semiconductors.

Mobility: The ease with which charge carriers can move through a semiconductor. Generally electrons and holes do not have equal mobility in a given semiconductor. Mobility is higher in germanium than in silicon.
MOS: A technology for producing transistors that incorporates metal-oxide-semiconductor layers. Electrical characteristics are similar to vacuum tubes.

Nonlinear: Having an output which does not vary in direct proportion to the input.

NP0: Denotes negative, positive, or zero (0) temperature coefficient of capacitance.

n-type semiconductor: An extrinsic semiconductor in which electron density exceeds hole density. An electron donor type.

Optoelectronics: Technology involving the use of devices having an electronic input and using light beams (photons) for such functions as amplification, switching, and coupling.

Passivation: The growth of an insulating layer on the surface of a semiconductor to provide electrical stability by isolating the transistor surface from electrical and chemical conditions in the environment. It reduces reverse-current leakage, increases breakdown voltages, and improves the power-dissipation rating.

Passive component: A component that does not provide rectification, amplification, or switching, but reacts to voltage and current; e.g., resistor, capacitor.

Permittivity: See dielectric constant.

Photoconductor: A passive, high-impedance device composed of thin single-crystal or polycrystalline films of compound semiconductor materials. When the sensitive surface is illuminated, its resistance decreases.

Photolithography: A photomechanical reproduction process which differs from offset printing only in that in photolithography the ink is transferred directly from the plate to the paper. Offset printing uses an intermediate transfer to a rubber roller; in both processes a halftone negative is made by photoengraving.

Piezoelectrics: Materials which have the ability to generate a voltage under the influence of a mechanical force, or to exert a mechanical force under the influence of an applied voltage; e.g., barium titanate, lead zirconate-titanate.

p-type conductivity: The conductivity associated with positive charges (holes) in a semiconductor.

p-type semiconductor: An extrinsic semiconductor in which the hole density exceeds the conduction electron density. An electron acceptor type.

Q: A figure of merit for an energy-storing device, tuned circuit, or resonant system. It is equal to the reactance divided by resistance. The Q of a capacitor, coil, circuit, or system determines the rate of decay of stored energy. The higher the Q factor, the longer it takes for energy to be released.

Resistance: That property of a conductor which determines the magnitude of the electric current which will pass through it at a given potential difference.

Resistivity: The resistance of a specimen of material of unit dimensions. Usual units are ohm-centimeters.

Seal: A structure in which two or more parts are joined forming a hermetically tight bond.

Semiconductor: A material with a resistivity intermediate between a conductor and an insulator. Its resistivity decreases with increasing
temperature, and is very sensitive to small additions of certain impurities. (See transistor.)

**Sputtering:** A method of depositing a thin film of material onto a substrate. The substrate is placed in a large demountable vacuum chamber having a cathode made of the metal or ceramic to be sputtered. The chamber is then operated so as to bombard the cathode with positive ions. As a result, small particles of the material fall uniformly on the substrate.

**TCC:** Temperature coefficient of capacitance.
**TCE:** Temperature coefficient of expansion.
**TCR:** Temperature coefficient of resistance.
**TCV:** Temperature coefficient of voltage.

**Temperature coefficient:** The factor by which a characteristic of a substance (e.g., resistivity, expansion) will vary in response to a change in its temperature.

**Thermionic:** Pertaining to the emission of electrons as a result of heat.

**Thermistor:** A semiconductor device, the electrical resistance of which varies with the temperature. Its temperature coefficient of resistance is high, nonlinear, and usually negative.

**Thermoelectrics:** Materials which can be used to convert thermal energy into electrical energy.

**Thick film:** A film with a thickness usually of the order of 10 to 100 \( \mu \text{m} \), applied by painting, dipping, screening, doctor blading, or similar processes.

**Thin film:** A film with a thickness usually of the order of less than 1 \( \mu \text{m} \), generally prepared by evaporation or sputtering. In practice, thick and thin films can overlap in thickness ranges.

**Transistor:** An active semiconductor device having three or more electrodes, and capable of performing almost all the functions of tubes, including rectification and amplification. Germanium and silicon are the main materials used, with impurities introduced to determine the conductivity type (\( n \)-type has an excess of free electrons; \( p \)-type, a deficiency).

**Varistor:** A two-electrode semiconductor device with a voltage-dependent nonlinear resistance which falls significantly as the voltage is increased.

**VCC:** Voltage coefficient of capacitance.
**VCR:** Voltage coefficient of resistance.
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