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ELECTROLYTIC PREPARATION OF HIGH DIELECTRIC THIN FILMS

by A. E. Hultquist and M. E. Sibert

Prepared under Contract No. NASw-969 *by*
LOCKHEED MISSILES & SPACE COMPANY
Palo Alto, Calif.
for

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FOREWORD

The work described in this report was carried out under Contract NASw 969 for NASA Headquarters, Washington 25, D.C. The program was directed toward the development of high dielectric thin films prepared by electrolytic techniques.

Acknowledgment is made to R.D. Wales, B.A. Traina, and R.D. Carpenter for their contribution to the process development portion of this study and to M. Honma, W.L. Ravenelle, and J. Robinson for their spectrographic and x-ray analysis of the films.

ABSTRACT

Several approaches toward the formation of high dielectric materials in thin film form by electrolytic techniques are considered, with emphasis on barium titanate. Some attention is devoted to zirconates, niobates, and tantalates. In addition to barium compounds, the comparable calcium, magnesium, strontium and potassium double oxides are evaluated by the appropriate electrolytic techniques. Rare earth double oxides are also considered, but dielectric properties are considered to be too marginal for inclusion in this study.

The basic technique employed is anodization of the applicable refractory metal with a simultaneous deposition or occlusion of the second oxide in the anodized film. Experiments are described applying this basic technique to aqueous electrolyte systems, organic electrolytes and gas phase systems. Molten salt systems were eliminated on the basis of excessive solubility of product oxide materials.

Films produced were evaluated in terms of pertinent capacitive and resistive properties. X-ray diffraction and spectrographic analyses are also reported for films of potential interest. It was demonstrated that appreciable amounts of barium and calcium could be incorporated in the films; strontium was not successfully codeposited.

The dielectric films as produced yield properties equivalent or slightly improved over simple anodized films. However, in the case of titanates and niobates, a subsequent vacuum heat treatment coupled with an air oxidation or healing step resulted in films with an order of magnitude improvement of capacitive properties and a consequent improvement in loss and resistive properties. Comparable results have not yet been achieved with zirconates and tantalates.

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Section 1
INTRODUCTION

The need for microminiature capacitive elements in thin film form for use in integrated circuitry has prompted this program. Presently developed thin film capacitive elements are largely amorphous structures of low dielectric constant and require relatively large thin film areas to obtain significant capacitances. The objective of this program was to develop procedures for the deposition of high dielectric materials in thin film form on suitable metal substrates to provide structures useful as capacitive elements. Capacitance values of the order of 2 to $5 \mu F/cm^2$ were a goal of this research.

The scope of this program includes a study of the parameters concerned with electrolytic film formation and evaluation of the films produced. The basic approach proposed for the preparation of these high-capacity elements entails the formation of a porous oxide film coupled with the deposition of a second phase so as to produce a double oxide composition. The porous oxide film is prepared electrolytically by anodizing a suitable metal substrate. The second phase is physically occluded in the porous film by the entrapment of ionic or finely particulate species during anodization. Electrophoretic processes can be employed as an aid in achieving the deposition of the second phase. This basic process can be applied to aqueous, organic, molten salt or gas phase electrolyte systems.

The choice of metal substrate and addition agents determine the final composite oxide and are determined by the presently available information on high dielectric compounds prepared by conventional ceramic techniques. Assuming dielectric constants on the order of 500 to 2,000, capacity values of 2 to $5 \mu F/cm^2$ may be attained on thin films of less than 1μ thickness. The work performed during the first year of this program under Contract NASw 765 served in part as a basis for the experimental program currently described (Ref. 1).

Section 2
MATERIALS CONSIDERATIONS

2.1 INTRODUCTION

Four basic electrolyte types were considered in this study: aqueous, organic, molten salt and gas phase. The basic process type, that of simultaneous anodization of a substrate metal coupled with deposition and/or occlusion of a second phase oxide, was applied to all of these. Emphasis was placed on a few aqueous systems because these produced the most promising results.

Each electrolyte type was evaluated in terms of preparation of titanates of the $A^{2+}B^{4+}O_3$ type (Perovskites). Because barium titanate is the best known in terms of chemical and electronic behavior, this material was the basic double oxide studied for most procedures. Promising approaches were also evaluated for niobates of the $AB^{5+}O_3$ type and zirconates of the $A^{2+}B^{4+}O_3$ type. Rare earth double oxides were also considered as potential high dielectric materials.

2.2 FILM MATERIALS

2.2.1 Double Oxides Based on Periodic Group IV-V Metals

As noted previously, the basic double oxide used for evaluation of most processes was barium titanate. The best procedures for each type process were then applied to comparable materials based on niobium and zirconium. A smaller amount of work was also devoted to comparable titanates, niobates and zirconates of calcium, magnesium, potassium and strontium. These encompass most of the known high dielectric materials based on the three selected refractory metals. Efforts to occlude the oxide of strontium were shown early to be unsuccessful, and this material was eliminated from further consideration in this study. After the rare earth double oxide materials were shown to be inapplicable to a high dielectric materials program, some studies were also run on comparable tantalates in lieu of the rare earth compounds.

2.2.2 Rare Earth Double Oxides

The rare earth elements are capable of forming double oxide species. These compounds have not been characterized as completely as the barium titanate or other Perovskite compounds; thus, information about them is not complete. The following classes of compounds have been considered:

- $A^{3+}B^{3+}O_3$ type
  A = rare earth configuration element
  B = Sc, Ti, V, etc.
- MO_2 Mixed Oxides (fluorites) $2A^{3+}2B^{4+}O_7$
  A = rare earth such as Ce, Pr, Tb
  B = Ti, Zr, etc.
- $A^{2+}12B^{3+}O_{19}$ (magneto-plumbite)
  A = Alkaline earth
  B = normally iron; partial or complete substitution by rare earth metal

Literature work revealed that very little electrical information concerning the rare earth oxides is available. The data in Table 1 are compiled from Landolt-Bornstein (Ref. 2).

The materials listed in Table 2 have been reported to possess interesting electrical properties, but none of the dielectric constants reported for these classes of materials are as striking as for the titanates, zirconates, niobates or tantalates. Therefore, in the experimental program tantalum was used as a fourth substrate rather than one of the rare earth metals.

Table 1

DIELECTRIC PROPERTIES OF SOME MATERIALS CONTAINING RARE EARTHS

Material	Form	Temperature (°C)	K
$LaScO_3$	Ceramic	20	30
$NdScO_3$	Ceramic	20	27
$NdAlO_3$	Ceramic	20	17.5
$CaCeO_3$	Ceramic	20	21
CeO_2	Ceramic	20	26
CeO_2	Film	RT	3.9
CeO_3	Ceramic	—	7
Y_2O_3	Ceramic	20	13

Table 2

PROPERTIES OF ADDITIONAL RARE EARTH MATERIALS

Material	Dielectric Constant	Reference	Remarks
$La_2O_3 - TiO_2$	40	6, 7, 8	
$Ce_2O_3 - TiO_2$	40	6, 7, 8	
$LaGaO_3$	15	4, 5	Discontinuity of temperature of transition (Curie Point?) 90—100°
$CeGaO_3$	—	4, 5	
$PrGaO_3$	—	4, 5	
$NdGaO_3$	—	4, 5	
$LaAlO_3$	15	4	
$NdAlO_3$	17.5	4	
La_2O_3		3	
$LaZrO_3$	24.9	9	
$NdZrO_3$	23.4	9	
$SmZrO_3$	20.5	9	

2.3 ELECTROLYTE MATERIALS

2.3.1 Aqueous Systems

Aqueous electrolyte systems were largely based on two types of baths. This selection was arrived at both on the basis of previous work on Contract NASw 765 and preliminary experiments carried out under the present program. The first of these basic bath types was a KOH solution containing particulate matter in the form of appropriate titanate, zirconate, niobate or tantalate. The second was an EDTA based system containing appropriate metal acetates. The second system was emphasized throughout the work since it exhibited the greatest potential for formation of a film dielectric material.

2.3.2 Organic Electrolyte Systems

Previous results obtained in this laboratory have lead to the tentative conclusion that anodic oxide films grow on titanium by transport of oxygen (or oxygen carrier) through the film to the metal-oxide interface (Ref. 1). Thus, other oxides may only be incorporated into the titanium oxide coating when the coating is porous or grown under such conditions that a polycrystalline coating is obtained. Attempts to incorporate a second oxide while forming a nonporous amorphous anodic film frequently fail because the titanium oxide is formed first and then a thin conducting coating of the second oxide is deposited on but not in the titanium oxide.

The best approaches to this problem seem to be either to form the high dielectric coating by incorporating a high dielectric material into a porous titanium oxidic coating by occlusion of electrophoretically moved particles, or by utilizing a titanium oxide anion to form a titanate on an anode of another metal such as cadmium, lead or barium.

2.3.3 Other Oxide Dielectric Materials

Several other oxide dielectric materials were briefly included in certain facets of the study due to specific applicability to a given process. These included the titanates of lead, tin and cadmium, together with a few survey experiments with the comparable zirconates and niobates.

In the case of the gas phase film formation, efforts were confined to experiments designed to produce the high dielectric rutile phase of titanium oxide. The brief time allotment for this phase of the program did not permit the detailed process analysis necessary for incorporation of a second phase material in the film.

To evaluate these approaches in an organic system, it is necessary to formulate a system containing the desired anions. Barium titanate of 200 to 500Å particle size has been prepared by solution precipitation techniques (Refs. 10, 11, 12). This material has good dielectric properties (Ref. 10), as shown below:

Q factor at 60 kV/cm		700
Breakdown voltage of a 1-mil film		400 V
Dielectric constant at	-40°C	550
	25°C	620
	150°C	640
	200°C	starts increasing

Dielectric constant drops precipitously above 25 V/mil

These techniques consist of either the addition of water to an alcoholic solution of titanium tetraethylate and barium methylate, or the addition of an alcoholic solution of a titanium ester (e.g., tetraisopropyl titanate) to an aqueous solution of barium hydroxide of pH 11 to 14. A simplified mechanism for the latter technique has been suggested (Ref. 12). Based upon the reaction

$$\begin{tikzcd}
Ti(OR)_4 + 4H_2O + Ba^{++} + 2OH^- \arrow[r] & Ti(OH)_6^{--} \arrow[d] + Ba^{++} + 4ROH \\
& BaTiO_3 + 3H_2O
\end{tikzcd}$$

an initial step is suggested involving the coordination of four water molecules and two hydroxyl groups through their oxygen to the titanium of the Lewis acid [$Ti(OR)_4$] in a nucleophilic process. One of the protons from each of the water molecules interacts with the oxygen of the alkoxide group to split off alcohol. The resulting anion, $Ti(OH)_6^{--}$, is considered to have a transient existence, stabilizing by undergoing condensation-polymerization with the release of water to form an infinite three-dimensional array of TiO_6 octahedra linked to six others through their corners. Because there are no discrete anionic groups in $BaTiO_3$, the condensation-polymerization is such that Ba + 3-0 together form a cubic close-packed arrangement in the TiO_6 array.

The hydrolysis of the titanate esters presents a unique opportunity for preparing a bath which contains titanium in the anionic form. If the $Ti(OH)_6^{--}$ ion or any hydrolysis ion is stable in a basic bath, then a method of preparing titanates should be possible. One approach would be the anodization of a cadmium or lead anode in the ester to form the appropriate titanates. Another possible method uses the basic isopropyl titanate bath with additions of barium hydroxide on other alkaline earth hydroxides. This latter bath could produce either a precipitate of the alkaline earth titanate which could be transported electrophoretically to the anode if charged correctly or a soluble titanate complex which would be electrochemically deposited.

2.3.4 Molten Salt Systems

The original program conceived anticipated utilization of molten salt systems for possible preparation of high dielectric thin films. These systems operating at elevated temperature would possess the advantage of providing for an in situ heat treatment to accelerate diffusive processes and promote crystal growth. After consideration of the literature background on molten salt systems together with preliminary experimentation, the probability of success for this approach appeared to be low, primarily due to the high solubility of all the applicable oxides in the salt systems. After conference with the project monitor, it was decided to devote this phase of the effort to expansion of the more promising aqueous systems.

2.3.5 Gas Phase Systems

This approach entailed carrying out the anodic film formation process in a glow discharge-produced vapor medium. To properly establish conditions for the process, the simplest system was selected. Thus, a water vapor-argon mixture was employed as the vapor "electrolyte." Some preliminary work was also done in air. This phase of the study was limited to survey work in order to more fully characterize the high dielectric materials produced in the aqueous systems phase of the program.

Section 3

FILM PREPARATION

3.1 SUBSTRATE MATERIALS

The types and grades of materials and the polishes used to prepare their surfaces are shown in Table 3. Although the materials obtained from Electronic Space Products, Inc., possess a bright finish, the chemical polish was applied routinely. Thus, all surfaces of each material were treated identically prior to anodization. Details of the chemical polish procedure can be found in the references indicated in the table.

Table 3

SUBSTRATE MATERIALS AND PRETREATMENT

Material	Purity	Polish	Reference
Ti	99.9	10 ml HF (48%) 60 ml H_2O_2 (30%) 30 ml H_2O	13
Zr	99.9	10 gm $NH_4BF_4 \cdot HF$ 40 ml HNO_3 20 ml H_2SiF_6 100 ml H_2O	14
Nb	99.9	1000 ml H_2SO_4 35 ml $Na_2Cr_2O_7$ (saturated)	1
Ta	99.9	50 ml H_2SO_4 20 ml HNO_3 20 ml HF(48%)	15

3.2 BATH PREPARATION AND ANODIZATION PROCEDURE

3.2.1 Liquid Electrolytes

All baths except the modified organic baths have been prepared using reagent grade materials and distilled water. The reagents used in the organic baths were technical grade. Bath stability was observed by comparing anodizing parameters with the resulting films as the bath was used over a long period of time. Evaluation of electrical properties of films formed in the EDTA-barium acetate bath was made and confirmed the observation that the basic aqueous systems employed were stable. Details of this study are found in a later section of this report. The modified organic electrolyte does develop a precipitate after about six samples have been processed.

Anodization was performed with a Kepco Model HB-8M power supply or a Lockheed-designed power supply. Both of these power supplies can be used either as a constant current or a constant voltage device.

After anodization, all films were rinsed with distilled H_2O and dried at 100°C for at least 1 hr before evaluation.

3.2.2 Gaseous "Electrolytes"

The gas anodization apparatus is shown in Fig. 1. Argon was used as a carrier gas for water vapor. The concentration of water in the gas stream was maintained by controlling the temperature of the water in the trap. Flow rates were controlled at the regulator on the argon tank. The internal electrodes made of the metal to be anodized, were spot welded to the tungsten leads and then coated with Dow 805 silicone to define the area of anodization. The gas is excited by an RF oscillator operating at about 3 to 10 megacycles frequency. The RF electrodes are attached on the outside of the gas inlet and outlet tubes. This is called a capacitive type arrangement. The elimination of contamination by internal RF electrodes is one of the major advantages of this technique.

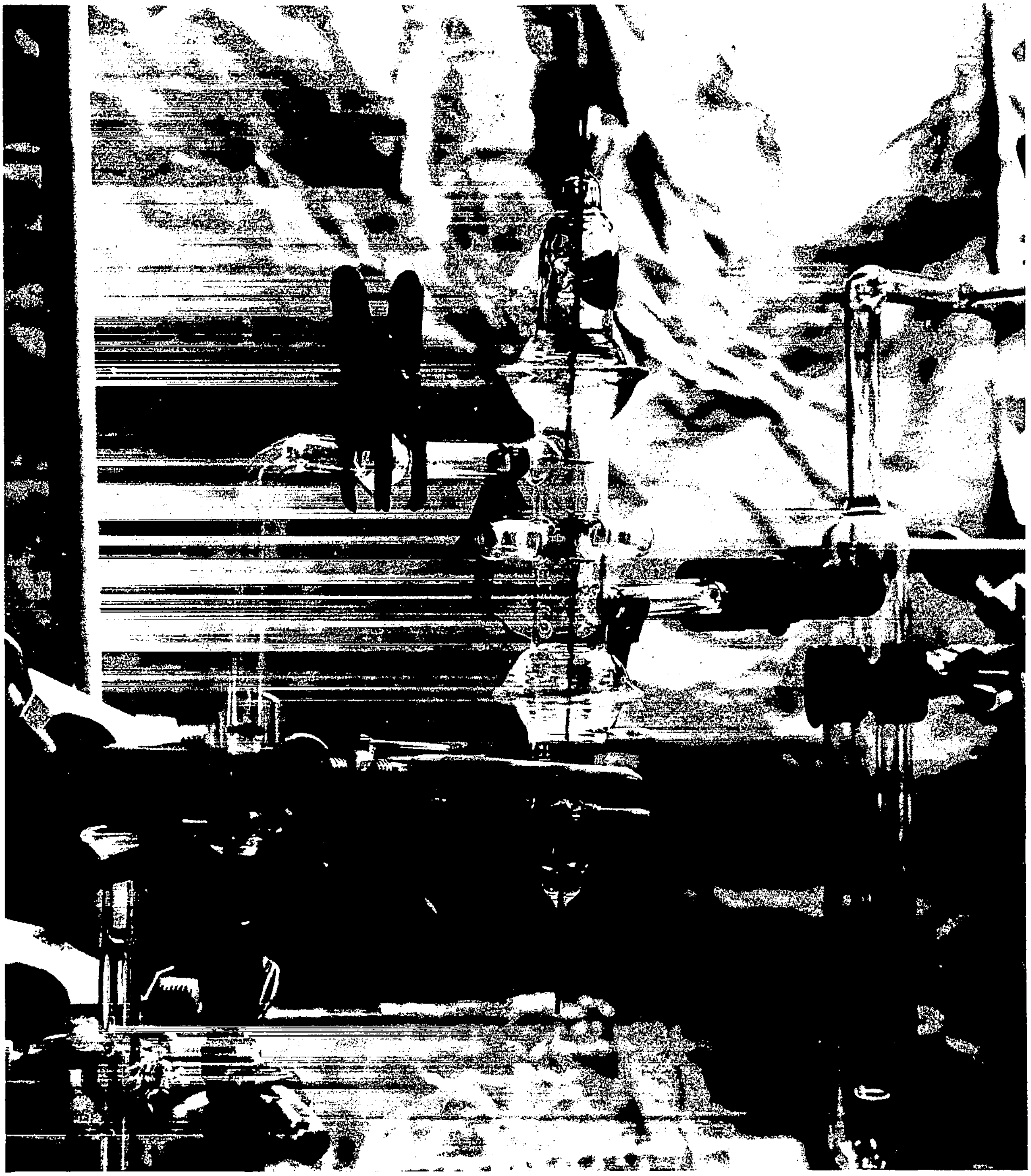

Fig. 1 Gas Anodization Apparatus

The gas is ionized in the glow discharge and the ions formed in the glow are attracted to the internal electrodes by the DC voltage applied to these electrodes. The amount of ionized ions depends upon the gas composition and pressure which are controlled by a manostat and read by a manometer, as well as the electrical energy induced in the gas by means of the high frequency electrical discharge.

The experimental arrangement shown was designed after several trial and error glow tubes were tested. This glow tube can be used with several RF electrode configurations and has proved quite versatile for the experiments performed at this time.

The procedure has been to achieve a steady state gas flow and then turn on the high frequency and set the glow. Then the anodization is initiated by imposing a DC voltage across the internal electrodes.

3.3 OCCLUSION OF PARTICULATE MATERIALS

Experiments conducted during the first year of this study indicated that electrophoretic deposits of $BaTiO_3$ could be made from several baths. However, the typical properties of electrophoretic coatings were observed in that they lacked good cohesion and adhesion. Attempts to improve these properties were not successful.

A combined electrodeposition-electrophoretic technique developed at this laboratory for NASA under Contracts NAS 8-1585 and NAS 8-11117 (Ref. 16) was selected as a possible method for forming high dielectric films. This technique is basically an anodization of the substrate in a slurry of the desired particles in an appropriate bath. The details of the fundamental processes involved have been discussed in the reports under that contract. A general description is as follows. To promote the migration of particles suspended in a bath, certain cation concentrations, notably H_3O^+, must be reduced to a low level. The refractory oxides and probably most refractory silicates and aluminates assume a positive charge in acid solutions due to the adsorption of this ion. To neutralize and make the particles negatively charged, a basic solution must be used. In basic solutions, the hydroxyl ion is adsorbed and the particles are made negative in charge. Thus, the particles can then be attracted to the anode which is positively charged. Along with the above requirement, it is necessary to exclude certain anions such as sulfates, chlorides, and nitrates which promote the transfer of electricity through the solution by other methods.

The system used in developing this technique was a slurry of TiO_2 or ZnO in a bath containing dissolved sodium aluminate. The substrate materials used were aluminum and aluminum alloys. Coherent and adherent coatings were obtained whose reflectance spectra showed the presence of the particular oxide used. The transition from those experiments to the present system involved both a change in substrate and a change in dispersed material from a simple oxide to a double oxide. Thus, extensive changes in bath and electrical conditions were anticipated.

Three baths were used in preliminary attempts to find an approximate applicable system. The bath compositions are found in Table 4.

Table 4

BATH COMPOSITIONS FOR DIRECT OCCLUSION PROCESS

Bath	KOH	Concentrations (gm/liter)		$BaTiO_3$ [(a)]
		$Ba(OH)_2$	$NaAlO_2$	
35-143	–	–	2.5	50
11-3	–	–	1.0	–
11-4	–	–	1.0	80
35-138	–	10	–	50
35-139	1.0	–	–	10
35-140	1.0	–	–	20
35-148	1.0	–	–	–
35-149	1.0	–	–	10
11-2	1.0	–	–	80
11-9	100.0	–	–	200

(a) $BaTiO_3$ is dispersed as a solid in the bath.

The results of these anodizations were as follows:

- In all systems with low base concentrations, a thin, non-porous, transparent film showing interference colors is grown upon which a thin layer of $BaTiO_3$ is deposited. The layer of $BaTiO_3$ is not adherent or coherent when dried.
- The capacitance data obtained on those samples, to which a counter electrode could be applied on the $BaTiO_3$, were the same as the capacitance data obtained for the clear, interference films formed in identical baths without $BaTiO_3$ present (about 0.025 $\mu F/cm^2$).
- Samples formed in the 10% KOH bath, bath 11-9, have shown surprisingly different characteristics. When current densities of 40 ma/cm^2 or greater are used, a gray, white film is formed which is adherent and coherent upon drying. Preliminary capacitance values of 0.35 $\mu F/cm^2$ were obtained.

Further experiments using the technique of occluding particulate matter in and on a titanium anodic film were directed toward determining the bath conditions necessary for formation of a continuous, coherent, and adherent film.

The results of these experiments are shown in Table 5. The best range of KOH concentrations was between 50 and 100 gm/liter. Concentrations greater or less than this range produce only translucent films or result in complete disintegration of the electrode.

Table 5

CONDITIONS USED IN THE PREPARATION OF FILMS CONTAINING HIGH DIELECTRIC MATERIAL

Bath Composition (gm/liter)		Anodization Parameters				Results
		Temp. (° C)	Final Voltage	Time (min)	Current Density (ma/cm^2)	
KOH	$BaTiO_3$					
25	200	25 – 100	90 – 100	7 – 17	15 – 175	Translucent – some patches of white
50	200	25 – 100	50 – 70	2 – 24	15 – 100	White to gray
75	200	25	55	7	175	White to gray
100	200	8 – 100	40 – 60	3 – 50	15 – 175	White to gray
150	200	25 – 100	40 – 45	7 – 30	100 – 200	Translucent – anode dissolves

Two other baths containing 200 gm/liter $BaTiO_3$ using different basic salts were used, one 30 gm/liter $Ba(OH)_2$ and the other 300 gm/liter potassium silicate. Although the latter bath produced a white film, the coating was very non-uniform. The $Ba(OH)_2$ bath did not produce a film with any indication of occlusion of the high dielectric material.

The $BaTiO_3$ used in these experiments has all been from the same source, and the average particle size is 0.5 to 3 μ. The hydrolysis of isopropyl titanate in the presence of barium and hydroxyl ions reportedly results in a finer particle size $BaTiO_3$ (Ref. 10). Some of the precipitate from such a hydrolysis has been used in a 75 gm/liter KOH bath. The films formed in this bath were not as thick or as white as those formed in the presence of the coarser $BaTiO_3$.

3.4 THE MODIFIED ORGANIC BATH

Some initial experiments were performed in which titanium was made anodic in an acetic anhydride bath developed in this laboratory for the anodization of germanium (Ref. 17). The electrical properties of capacity and loss were similar to those observed for titania films made in aqueous baths. Rather than approach the anodization of titanium in an organic electrolyte in a conventional manner, a fresh approach utilizing a combination of electrophoresis and anodization was proposed. The technique consists of hydrolyzing the isopropyl titanate ester in isopropyl alcohol. This can be done with or without the presence of barium hydroxide with tetraethyl ammonium hydroxide.

When tetraethyl ammonium hydroxide is added to an alcoholic solution of isopropyl titanate, a precipitate is formed which redissolves upon standing. The dissolving of this precipitate suggests the solution of $Ti(OH)_6^{--}$. The material deposited at the anode from such solutions has been analyzed by x-ray. The results for one sample indicated about 40% crystalline material. This crystalline material was composed of about 60% rutile TiO_2 and 40% anatase TiO_2.

It was found that, for low to medium concentrations of the above basic solutions, the addition of barium hydroxide (aqueous solution) results in the formation of a precipitate which apparently redissolves. Because the conductivity of this solution was found to be greatly decreased, it is suggested that one of the following conditions apply:

(1) A complex hydroxyl anion of $BaTiO_3$ is obtained.
(2) An extremely small negatively charged particle of $BaTiO_3$ is formed.
(3) An uncharged molecule or positively charged particle or molecule is formed.

Attempts have been made to deposit titania or barium titanate in actively growing anodic films. A summary of the conditions and baths used are found in Table 6. The isopropyl titanate was technical grade and was obtained from the DuPont Company. The tetraethylammonium hydroxide was also technical grade, 10% by weight, in an aqueous solution obtained from Eastman Organic Chemicals. Substrates used included titanium, lead, cadmium, and platinum.

Table 6

PREPARATION OF FILMS IN HYDROLYZED ISOPROPYL TITANATE BATHS

Bath Composition (gm/ml)				Anodizing Conditions		
Isopropyl Titanate	Tetraethyl-Ammonium Hydroxide	$Ba(OCH_3)_2$	$Ba(OH)_2$ $0.8\ H_2O$	Time (min)	Temp. (°C)	Current Density (ma/cm^2)
0.2 to 8.0	0.1 to 5.0	0.25 to 1×10^{-2}	2.8 to 7.0×10^{-4}	2–20	8–100	3–200

3.5 PREPARATION OF FILMS IN THE EDTA BATH

A bath was developed during this program to codeposit alkali and alkaline earth atoms in growing anodic films. The codeposition is achieved by complexing the alkali or alkaline earths as the ethylenediaminetetraacetic complex in a weakly basic solution of boric acid. The bath formulations used are shown in Table 7. In addition to the alkali and alkaline earths, lead has been complexed in this bath. Anodizations of

Table 7

BATH FORMULATIONS AND PROCESSING CONDITIONS USED IN PREPARING FILMS IN EDTA-ALKALI METAL ACETATE AND LEAD ACETATE BATHS

Bath Composition (gm/liter)				Anodizing Conditions			
Source Material	EDTA	H_3BO_3	KOH	Time (min)	Temp. (°C)	Current Density (ma/cm^2)	Final Voltage
Barium Acetate							
22	30	5.0	20	45	25-35	40	240-260
31.5	43	7.15	14.3	12-50	25-100	50-100	160-240
31.5	43	7.15	28.6	0.5-152	25-100	50-100	70-240
Calcium Acetate							
21.5	43	7.15	14.3	4-30	25-100	5-200	120-315
Strontium Acetate							
26.5	38.5	6.5	13	1-10	20-40	100-200	195-320
Strontium-Barium Acetate							
	38.5	6.5	13	1-10	20-40	100-200	200-300
Potassium Acetate							
26.5	38.5	6.5	13	1-45	20-40	25-100	200-260
Sodium Acetate							
26.5	38.5	6.5	13	4-25	25-55	20-100	220-320
Lead Acetate							
21.5	43	0-7.15	0-28.6	8-22	25-60	50-100	50-170

titanium, zirconium, niobium, and tantalum have been performed in these baths. Under the conditions indicated in the table complexing of the metal ions in a negatively charged complex is necessary to attract and deposit the metal at the positively charged anode. The bath pH is, in general, adjusted to maintain an environment stable enough to prevent decomposition on standing but permitting decomposition of the complex when an electric field is present. A complete and detailed study of how this bath operates was beyond the scope of this contract. However, observations have been made with particular systems providing some indication of the physical and chemical characteristics of the films as well as their electrical properties, which indicate that the conditions chosen in at least some of these experiments produced the desired film.

3.6 GAS ANODIZATION FILMS

Oxide coatings have been formed on titanium by anodization in a glow discharge of argon and water vapor. They have been preformed at pressures between 1 and 10 mm Hg, with argon flow rates of approximately 25 cm/min, ice vapor pressures of 5.6×10^{-4} and 0.77 mm Hg, and anodization voltages of 50, 100, 150, and 250 V. Less than 25 experiments were performed with this technique. The results and indicated potential of this approach are described in Section 4.

Section 4
DIELECTRIC FILM EVALUATION

4.1 INTRODUCTION

The films produced by the methods described in Section 3 have been evaluated for visual uniformity, chemical composition, and crystallinity by spectrographic and x-ray analysis. Thickness has been measured with a Dermitron thickness gage, and their electrical properties of dry and wet capacitance, loss factor, frequency, and temperature dependence of the capacitance and DC resistance have been determined. All of these techniques have been used on those films which showed interesting electrical properties, while other films possessing less interesting properties have been investigated less exhaustively.

The routine measurements of capacitance have been made with a General Radio Impedance Bridge Model 650A. This bridge operates at 1 kc, and a signal level of 0.10 V has been routinely applied. The evaluation of capacitance at other frequencies was made on this bridge using an external signal of the same level. The signal was provided by the Hewlett-Packard Audio Signal Generator Model 206A. Routine DC resistance measurements were made on a Kiethly Model 610 Voltmeter-Ammeter. This instrument is a controlled constant current device which avoids breakdown of the film due to the passage of large current in uncontrolled devices. The x-ray and spectrographic analyses were performed with standard General Electric and Jarrel-Ash equipment, respectively. The thickness measurements were made on a Dermitron thickness gage where possible and were also checked several times against micrometer measurements, on thicker samples. Thickness determinations for very thin translucent films were made using the interference scale developed under the previous contract NASw 765.

This section presents separately the observations on films formed in each bath type. The various substrates used, modifications of the bath, and additional processing approaches are also included.

4.2 THE OCCLUSION OF PARTICULATE MATERIAL

4.2.1 Composition and Crystallinity of the Films

White films formed in the KOH-$BaTiO_3$ bath have been analyzed both spectrographically in terms of semiquantitative analysis for metal constituents and by x-ray diffraction to determine if appreciable amounts of crystalline $BaTiO_3$ were present in the film. The spectrographic analysis showed major amounts (greater than 10%) of titanium and barium. The x-ray analysis showed only two lines at d values of 2.85 and 2.83 which correspond to the major lines for $BaTiO_3$. No other lines were observed. Thus, solid $BaTiO_3$ can be incorporated in a growing anodic film on titanium.

4.2.2 Electrical Measurements

4.2.2.1 Effect of Moisture

Capacitance measurements using Ag-Aquadag and mercury counter electrodes were made on a sample whose film was adherent and uniform with a thickness of 67 μ. Capacitance values were obtained at room temperature and room humidity and in a dessicator with Drierite used as the dessicant. The values are typical of all the films formed in the KOH-based bath. The capacitance in room humidity was 0.5 $\mu F/cm^2$ and over drierite the capacitance was $1.9 \quad 10^{-4}$ $\mu F/cm^2$. Even films which are vacuum heat treated and air oxidized retain this sensitivity to moisture (see Table 9).

4.2.2.2 Surface Conductivity

Capacitance was measured using mercury electrodes of two different film areas. The ratio of capacitance of the large electrode to the small electrode was 3.65 which is in good agreement with the ratio of the areas of about 4.6. Thus, little surface conductivity is associated with the coating.

4.2.2.3 Capacitance-Temperature Relationship

Typical capacitance values and effective dielectric constants from room temperature to 150°C are shown in Table 8. There is a very large drop in capacitance as the sample is heated to 50°C. As a function of temperature there is a rise in the capacitance and effective dielectric constant of the sample, with an apparent maximum around 110°C. This is typical behavior for barium titanate, but the low value of the dielectric constant indicates that the barium titanate is either present is small amounts, or that the composite nature of the coating, which probably includes TiO_2 and K_2O, modifies the electrical characteristics extensively.

4.2.3 Vacuum Heat Treatment

Sample coatings prepared in a KOH-$BaTiO_3$ bath were placed in quartz tubes and evacuated to 5 μ Hg. They were placed in an oven at 600°C for 15 min, removed, and cooled. Remeasurement of these samples was made; then the samples were reoxidized in an air oven at 200°C or higher. The capacitance and losses are shown in Table 9. No improvement in the electrical properties of these coatings was observed.

4.2.4 Conclusion

Coatings formed in the KOH-$BaTiO_3$ bath have been shown to contain some $BaTiO_3$. However, the complex nature of the coating which includes considerable moisture masks the electrical properties of the occluded $BaTiO_3$.

Table 8

TEMPERATURE CHARACTERISTICS OF KOH-$BaTiO_3$ COATINGS

Temperature (°C)	Capacitance Measurement[a] ($\mu F/cm^2$)	Dielectric Constant Measurement
25	0.390	29,500
50	0.0013	98
70	0.0018	135
95	0.0024	180
110	0.0032	240
120	0.0019	145
150	0.0018	135

(a) Capacitance values are in terms of C_s.

Table 9

VACUUM HEAT TREATMENT OF KOH-$BaTiO_3$ FILMS

	Capacitance[a] ($\mu F/cm^2 \times 10^3$)						Loss					
Sample 11-97	C	E	F	G	H	I	C	E	F	G	H	I
Initial	8.1		8.3	9.3	9.8	5.3	2.2	2.2	2.6	2.3	2.3	1.7
Vacuum Heat Treated 600°C – 15 min	0.25	2.0	N.M.[b]			N.M.	3.8	2.4	N.M.			N.M.
Air Oxidized 200°C 16 hr	9.1	24.5	N.M.			N.M.	3.4	2.4	N.M.			N.M.
Air Oxidized 300°C 2-1/2 hr	32.5	13.7	18.2			9.1	1.3	2.4	1.7			1.8
Air Oxidized 200°C 4-1/2 hr	8.8	7.0	5.6			7.1	3.3	3.3	2.9			2.7
Over Drierite			0.50						0.02			

(a) Capacitance is C_p value except sample F over drierite.
(b) N.M. – not measured.

4.3 THE MODIFIED ORGANIC BATH

4.3.1 Description and Composition of Films

The types of films formed can be generalized for all experiments conducted. On platinum, a thin white non-adherent film was formed. On cadmium and lead two films are formed. From visual inspection the film adjacent to the substrate consists primarily of the oxide of the substrate and is, in general, very adherent to the substrate. The other film is formed over this oxide and adjacent to the solution. This film is hydrolyzed isopropyl titanate and is characteristically colorless when wet and dries to a white non-adherent film. All the results observed so far indicate that the two films are not connected by any chemical bond, and there is little if any mixing of the two oxides.

The inspection of films formed on titanium indicates that again the oxide derived from the substrate does not mix appreciably with the oxide derived from the anodizing solution. The oxide film formed by hydrolysis during the anodization is not adherent to the oxide obtained from the substrate.

The x-ray analysis of stripped films is shown in Table 10. The film is apparently a mixture of anatase and rutile TiO_2.

Table 10

X-RAY ANALYSIS OF FILMS FORMED
IN MODIFIED ORGANIC BATH

Observed Lines		Anatase		Rutile	
d	I/I_o	d	I/I_o	d	I/I_o
3.52	100			3.51	100
3.26	58	3.26	100		
2.49	35			2.49	
2.36	24	2.38			
2.19	18.5	2.19			
1.90	47				
1.69	70				
1.67	35				
1.63	18				

4.3.2 Electrical Measurements

Due to the cracking of these films on drying, only minimal capacitance measurements were made. Because thickness values could not be reliably determined, no effective dielectric constant can be calculated. Capacitance values were 0.019 to 0.044 $\mu F/cm^2$. The apparent loss was about 0.022.

4.3.3 Conclusions

Films of TiO_2 can be produced on anodic metal substrates in a basic, partially hydrolyzed isopropyl titanate bath. Under the conditions employed very little adhesion was obtained between the depositing oxide film and the oxide film produced by anodization of the metal. The deposited oxide film exhibited very serious cracking and crazing upon air drying. Both of these obstacles would have to be overcome before these films would be of any practical use. A vacuum heat treatment could possibly improve the overall characteristics of these films.

4.4 GAS ANODIZATION

4.4.1 Introduction

The purpose of the gas anodization experiments was to develop a technique and experimental apparatus to prepare anodic films on titanium. The initial experiments were conducted with four internal electrodes. Various assemblies using two external electrodes for the RF power input to ionize the gas were made. The final reactor assembly was described in an earlier section.

The experiments performed in this apparatus are shown in Table 11. All experiments were run at 2 mm Hg pressure in the system. Argon was passed over ice at a temperature produced by solid CO_2-acetone and an ice-salt mixture. These two temperatures (-78 and -20° C) provide water vapor pressures of 5.6×10^{-4} and 0.776 mm Hg, respectively. Water was used as a source of oxygen in anticipation of hydrolyzing +3 and +5 metal chlorides or organic compounds to form doped anodic films.

Table 11

GAS ANODIZATION EXPERIMENTS

Run	H_2O Vapor Pressure (mm Hg)	Film Thickness (Å)	DC Voltage (V)	Initial Current (ma)	Final Current (ma)	Time (min)
C	5.6×10^{-4}	360	200	0.9		135
G-1	0.776	425	200	4.2	2.65	220
G-2	0.776	460	250	5.0	3.4	308
G-3	0.776	100	50	0.50	0.32	88
G-4	0.776	200	100	1.28	1.26	179
G-5	0.776	300	150	2.4	2.1	239
G-6	0.776	380	250	5.6	4.15	

The capacitance and loss of one anodic film whose thickness was approximately 425 Å was found to be 0.015 $\mu F/cm^2$ and 0.029 respectively. These values are similar to those obtained with liquid electrolytes.

The technique does show promise for preparing thin films of oxides on metals. The process is slow enough to allow modification of the film by introducing hydrolyzable or oxidizable materials in ths gas stream. Control of process parameters is convenient.

The experiments G-1 and G-2 are not comparable because the position of the anode in the glow was not the same. The series G-3 through G-6 are comparable. Additional experiments were made using nickel wire mesh cathodes placed very close to the anode. In this case the anodic coating was not uniform and current values were not raised as anticipated using this geometric configuration.

4.5 THE EDTA-METAL ACETATE BATHS

4.5.1 Introduction

Considerable effort has been made to develop a coating process from this bath. The presence of major amounts of barium in the films has spurred interest, and methods of crystallizing the films to develop the high dielectric state have been investigated. The metal acetates primarily used have been the alkali and alkaline earth metal acetates. This section describes experiments and films formed in baths containing these acetates. The alkali and alkaline earth niobates, tantalates, titanates, and zirconates are among the most common high dielectric materials of the Perovskite type.

4.5.2 Composition of Coatings

The coatings were stripped in a bromine-methanol solution which dissolves the metal without attacking the oxides. The coatings were then submitted for semiquantitative analysis by a mass spectrograph. A more detailed analysis of the coatings is not included in the scope of this work. Any further work should include a detailed analysis and correlation of the composition with process parameters.

The results are shown in Table 12. The scatter of the results is large, but the amount of barium in the film increases with the anodization time. Also the bath containing strontium did not function properly and strontium was never detected in any of the films.

The EDTA did not complex the strontium, and a precipitate formed which was probably strontium hydroxide.

4.5.3 X-Ray Analysis

Samples of coatings formed on titanium in EDTA-barium acetate baths were analyzed by x-ray diffraction without stripping from the substrate. The data are shown in

Table 12

SPECTROGRAPHIC ANALYSIS OF FILMS FORMED ON Ti, Zr, Nb AND Ta IN EDTA METAL ACETATE BATHS (Current Density 100 ma/cm^2)

Sample	Metal Acetate	Anodizing Time (min)	Bath Temperature (°C)	Coating(a) Condition	Spectrographic Analysis		
					Major	Minor	Trace
Substrate Titanium							
11-27-E	Ba	12.5	24–42	A. P.	Ti, Ba	Si	Al, Mg, B
11-74-C	Ba	2	23–28	A. P.	Ti	Ti	Ba, Si, Fe
11-74-D	Ba	2	28–30	A. P.	Ti		Ba, Si, Fe
11-75-C	Ca	2	24–34	A. P.	Ti, Ca		
11-75-D	Ca	2	30–36	A. P.	Ti, Ca		
11-76-C	Sr	2	30–35	A. P.	Ti		
11-76-D	Sr	2	24–26	A. P.	Ti		
11-77-C	Ba, Sr	2	28–28	A. P.	Ti, Ba	Ca, Fe	Mg
11-77-D	Ba, Sr	2	27–29	A. P.	Ti, Ba		
11-82-C	Ba	5	30–39	A. P.	Ti, Ba	Ca, Zr	
11-82-D	Ba	10	24–34	A. P.	Ti, Ba	Ca	Ni
11-107-A	Ba	10	21–31	A. P.	Ti	Ba	
11-107-C	Ba	10	20–30	A. P.	Ti, Ba		
11-107-E	Ba	5	20–35	A. P.	Ti, Ba		
11-107-G	Ba	5	19–34	A. P.	Ti	Ba	
11-107-I	Ba	2	26–28	A. P.	Ti	Ba	
11-107-K	Ba	2	26–28	A. P.	Ti	Ba	
11-107-B	Ba	10	18–34	V. H. T.(b)	Ti	Ba	
11-107-D	Ba	10	20–35	V. H. T.	Ti	Ba	
11-107-F	Ba	5	24–35	V. H. T.	Ti	Ba	
11-107-H	Ba	5	22–30	V. H. T.	Ti, Ba		
11-107-J	Ba	2	25–28	V. H. T.	Ti	Ba	
11-107-L	Ba	2	22–26	V. H. T.	Ti, Ba		
11-111-A	Ba	10	22–34	V. H. T. & O.(c)	Ti, Ba		
11-111-B	Ba	5	22–32	V. H. T. & O.	Ti, Ba		
11-111-E	Ba	5	24–31	V. H. T. & O.	Ti, Ba		
11-111-F	Ba	5	22–34	V. H. T. & O.	Ti, Ba		
11-111-I	Ba	2	17–23	V. H. T. & O.	Ti, Ba		
11-111-J	Ba	2	20–24	V. H. T. & O.	Ti	Ba	
Substrate Zirconium							
11-74-E	Ba	2	30–35	A. P.	Zr		Ba, Si
11-74-F	Ba	2	27–34	A. P.	Zr		Ba, Si
11-75-E	Ca	2	30–39	A. P.	Zr, Ca		
11-75-F	Ca	2	24–34	A. P.	Zr, Ca		
11-76-E	Sr	2	30–34	A. P.	Zr		
11-76-F	Sr	2	24–26	A. P.	Zr		
11-77-E	Ba, Sr	2	28–32	A. P.	Zr, Ba		Ni
11-77-F	Ba, Sr	2	28–30	A. P.	Zr, Ba		Ni
Substrate Niobium							
11-74-H	Ba	2	28–35	A. P.	Nb, Ba	Si	
11-75-G	Ca		26–32	A. P.	Nb, Ca		
11-75-H	Ca		27–34	A. P.	Nb, Ca		Ti
11-76-G	Sr		26–28	A. P.	Nb		
11-76-H	Sr		24–29	A. P.	Nb		
11-77-G	Ba, Sr		27–29	A. P.	Nb, Ba	Ca	
11-77-H	Ba, Sr		23–27	A. P.	Nb, Ba	Ca, Zr	Ni

(a) A. P. – As produced coatings.
(b) V. H. T. – Vacuum heat treated – not oxidized.
(c) V. H. T. & O. – Vacuum heat treated – oxidized.

Table 13. Surprisingly, the as-produced films are crystalline and are made up of both the anatase and rutile forms of TiO_2. The barium oxide, if present, is too small to be seen or is not crystalline. The heat-treated films do not show any striking changes except that two of the three samples show a weak broad peak at about 3.95. The data here are not good enough to form any conclusion concerning the presence of $BaTiO_3$. A much more detailed study should be made to answer this question.

An alternate explanation of the electrical properties is that a structure has been developed in the heating process. However, there are not sufficient data here to determine if any change in structure has occurred as a result of the heat treatment. The films strip very smoothly and should make ideal samples for an experimental study.

Samples of the zirconium-based films prepared in a calcium acetate bath were also analyzed by x-ray diffraction. The bath used was slightly different than those described for titanium in that the calcium acetate concentration was about 22 gm/liter. One sample was heated in air for one hour at 500° C. The data are shown in Table 14. Both the heat-treated and as-produced samples are crystalline and are a mixture of the monoclinic, cubic and tetragonal forms. Heat treatment causes a few lines to disappear and some new ones to appear.

4.5.4 Electrical Properties — EDTA Films

4.5.4.1 Introduction

Electrical properties of wet and dry capacitance, dissipation factor, and DC resistance have been evaluated. The reproducibility, effect of bath type, and anodization time have been determined using as-produced films. A study of the effect of air and vacuum heat treatment on electrical properties has been performed. Film thicknesses have been taken for use in calculating an effective dielectric constant. The effect of frequency and temperature on the capacitance has been observed.

Table 13

X-RAY DATA – FILMS FORMED IN EDTA-BARIUM ACETATE BATHS ON TITANIUM AS PRODUCED AND HEAT TREATED

As Produced	Observed Lines								Known Lines					
Sample	11-2S		11-111L		11-111-G		11-111-D		Rutile		Anatase		$BaTiO_3$	
	d	I/I_o	d	I/I_o	d	I/I_o	d	I/I_o	d	I/I_o	d	I/I_o	d	I/I_o
			3.50	100	3.51	100	3.50	100			3.51	100	4.03	12
	3.22	100	3.24	100	3.25	100	3.24	100	3.245	100			3.99	25
			2.47	40	2.48	43	2.47	50	2.489	41			2.838	100
							2.45	87			2.435	9	2.825	
					2.38	47					2.379	22	2.314	46
											2.336	9		
									2.297	7				
					2.18	31	2.17	43	2.188	22				
									2.054	9			2.019	12
					1.88	32	1.88	38			1.891	33	1.997	37
											1.699	21		
			1.68(a)		1.68(a)		1.68(a)		1.687	50				
Unknown Lines			3.37		3.58						1.665	19		
Vacuum Heat Treated and Oxidized			3.9	V.W.			3.94	W.						
			3.51		3.52		3.50							
			3.245		3.25		3.24							
			2.48		3.02		2.48							
			2.07		2.48		2.189							
			1.89		2.18		1.87							
					1.89		1.62							
					1.69		1.36							
					1.68									

(a) Ti line interferes with possible TiO_2 lines.

Table 14

X-RAY DATA – FILMS FORMED ON ZIRCONIUM IN THE EDTA BATH CONTAINING COMPLEXED CALCIUM

As Prepared		Heat Treated (500°C–1 hr)		Baddeleyite Monoclinic		Tetragonal		Cubic	
d	Intensity	d	Intensity	d	I/I_o	d	I/I_o	d	I/I_o
				5.05	5				
4.10	VW								
				3.69	15				
3.62	W	3.62	W	3.63	12				
3.15	M	3.15	M	3.16	100				
2.93	S	2.93	S			2.92	100	2.93	100
2.80	M	2.80	M	2.84	65				
				2.62	20				
				2.60	12				
2.55	M	2.55	M	2.54	15	2.52	40	2.53	60
				2.50	3				
2.32	W			2.33	5				
		2.20	W	2.21	10				
				2.19	5				
2.18	W			2.18	5				
		2.00	W	2.02	7				
				1.990	7				
				1.846	15				
				1.817	20	1.81	60		
1.80	S	1.80	S	1.802	12			1.80	100
				1.781	5	1.79	100		
		1.68	VW	1.693	10				
				1.655	12				
1.64	W	1.64	W	1.642	7				
				1.609	5				
				1.591	5				
				1.581	5				
						1.55	50		
1.54	S	1.54	M	1.542	10	1.53	100	1.53	100
				1.508	5				
				1.495	5				
1.47	M	1.47	W	1.477	10	1.47	60	1.464	30
				1.449	3				
1.42	VW	1.41	W	1.420	7				
				1.360	2				
				1.32	5				
						1.29	40		
1.275	VW	1.28	VW	1.262	5	1.27	60	1.267	30
				1.246	2				
				1.213	2				
1.175	M	1.17	M			1.17	40		
						1.16	70	1.164	30
1.143	M	1.14	W			1.13	40	1.133	30
						1.10	60		
						1.05	40		
1.045	M	1.04	M			1.04	70	1.035	30
0.985	M	0.985	W			0.993	40		
						0.978	70	0.967	30
0.905	VW								
								0.8968	20
0.865	M	0.866	W						
0.853	VW	0.853	W					0.8575	30
								0.845	20
								0.802	20

(a) Intensity Code: S = Strong, M = Medium, W = Weak, VW = Very Weak

4.5.4.2 Reproducibility of Capacitance

To evaluate the electrical data, it is necessary to know the spread of values that might be obtained from a bath. To establish this range, a series of nine samples on titanium substrates from the same barium bath were run at the same conditions, namely 100 ma/cm^2 current density for five minutes at 22 to 30° C. Four silver counter electrodes were painted on the sample and the capacitance measured. The data are presented in Table 15. Three of the nine samples consistently average about 1/2 the average of the other six. Agreement between capacitance values obtained from the electrodes on any one sample is quite good. Inspection of the formation data has failed to disclose the reason for the low capacitances of these three samples.

Table 15

REPRODUCIBILITY OF CAPACITANCE VALUES

Anodizing Conditions:	100 ma/cm^2	current density
	22−30° C	bath temperature
	5 min	anodizing time
	barium	bath type
	titanium	substrate

Values are nF/cm^2

Sample 11−85

Electrode	A	B	C	D	E	F	G	H	I
1	25.0	20.1	26.9	9.3	9.8	19.3	22.8	17.6	9.6
2	17.6	16.7	14.2	7.4	9.8	18.1	19.8	19.9	
3	19.6	19.1	21.6	8.1	10.5	14.7	24.5	20.1	8.8
4	19.3	19.1	18.6		8.6		21.3	18.6	
Average	20.4	18.1	20.3	8.3	9.7	17.4	22.1	19.0	9.2

4.5.4.3 Effect of Bath Type and Anodization Time

A comparison of capacitance values for films produced in four bath types is shown in Table 16. Allowing for slight differences in preparation noted in the data, the values

Table 16

EFFECT OF BATH TYPE

Substrate	Bath Type	Current Density (ma/cm^2)	Time (min)	Temp. (°C)	Final Voltage (V)	Capacitance (nF/cm^2)	Dissipation Factor	Thickness (μ)
Titanium	Barium	100	5	22−37	230	8.3 to 22.1	0.11 to 0.34	3
	Calcium	100	5	23−34	250	8.1	0.13	5
	Strontium	100	5	25−29	250	5.9	0.08	
	Barium Strontium	100	2	26−32	200	22.6	0.14	
Zirconium	Barium	100	1	26−28	280	5.4	0.026	
	Calcium	100	2	24−29	320	3.5	0.025	
	Strontium	100	2	26−35	310	3.3	0.036	
	Barium Strontium	100	2	23−30	300	3.9	0.028	
Niobium	Barium	100	2	36−24	250	9.3	0.12	6
	Calcium	100	2	32−27	260	6.9	0.062	8
	Strontium	100	2	21−27	260	6.0	0.045	10
	Barium Strontium	100	2	24−28	260	6.15	0.057	9
Tantalum	Barium	100	2	24−30	290	12.5	0.082	4
	Calcium	100	2	24−27	290	9.8	0.125	4
	Strontium	100	2	21−27	300	15.8	0.076	5.6
	Barium Strontium	100	2	24−28	290	10.5	0.10	4

from all baths on any particular substrate are identical. The presence of barium, calcium, or probable absence in the case of samples prepared in the strontium bath does not influence the capacitance at least in unfired films.

The effect of anodization time on the capacitance and thickness of the film is shown in Table 17. In this one study, only tantalum was used as the substrate. It is evident that the capacitance decreases and the film thickness increases with anodization time.

Table 17

EFFECT OF ANODIZATION TIME

Bath Type	Anodization Time (min)	Capacitance (nF/cm^2)	Dissipation Factor	Thickness (μ)
Barium	2	8.6	0.073	6.6
	4	5.3	0.082	13
	5	4.2	0.071	13.5
Calcium	2	9.1	0.085	6
	4	5.4	0.058	9
	5	4.9	0.069	13.5
Strontium	2	15.4	0.040	4.5
	4	7.8	0.043	8
	5	4.1	0.047	18
Barium Strontium	2	8.8	0.10	6.5
	4	4.6	0.085	12
	5	2.9	0.061	15

4.5.4.4 Heat Treatment of Films in Air

Samples of titanium and zirconium were anodized in the four baths at 100 ma/cm^2 for one minute or 200 ma/cm^2 for 0.5 min. The capacitance was measured as a function of temperature and electrical resistance of the films. Samples were then placed in an air oven at 950° F (510° C) for various lengths of time. The temperature-capacitance curve and the electrical resistance were redetermined. A typical temperature-capacitance curve is shown in Fig. 2. The heat treatment lowers the capacitance and the temperature coefficient of the capacitance up to about 100° C for the films formed on both titanium and zirconium. These results are typical of films formed on titanium in all baths. Prolonged heat treatment of the zirconium films completely destroys the capacitance properties. The dissipation factor is lowered slightly which would be expected with the lowering of the capacitance.

There is no indication of titanate formation due to this heat treatment. The results of spectrographic analysis for the films indicate that the correct forming conditions may not have been used, and the films had little or no metal deposited from the solution. Some representative resistance values (in MΩ) before and after heating are shown in Table 18, at several applied voltages. The resistance of the titanate films is changed little if any by this heat treatment while the zirconium films show large increases in resistance. Measurement of the resistance of the heated metal was made to determine if the large resistance could be attributed to the substrate. The results show this to be true. Thus, the heated anodic film is probably conductive. It is not feasible to perform heat treatments in air at any higher temperatures due to excessive oxidation of the metal. The air heat treatment can possibly be used as a final step in a series of heat treatments in which a reduced oxide film is obtained.

Table 18

RESISTANCE OF FILMS – AIR HEATED

Substrate	Sample Bath	Before Heat (MΩ)			After 8-hr Heat Treatment (MΩ)			
		2	4	6	2	60	80	100
Titanium	11-55-D	1			1			
Titanium	11-58-D	10	1	1	20	2	1	
Titanium	11-58-C	3	1	1	20	1.5	1	
Zirconium	11-59-G	5×10^4	10^4	1	10^5	10^5	3×10^4	5×10^3

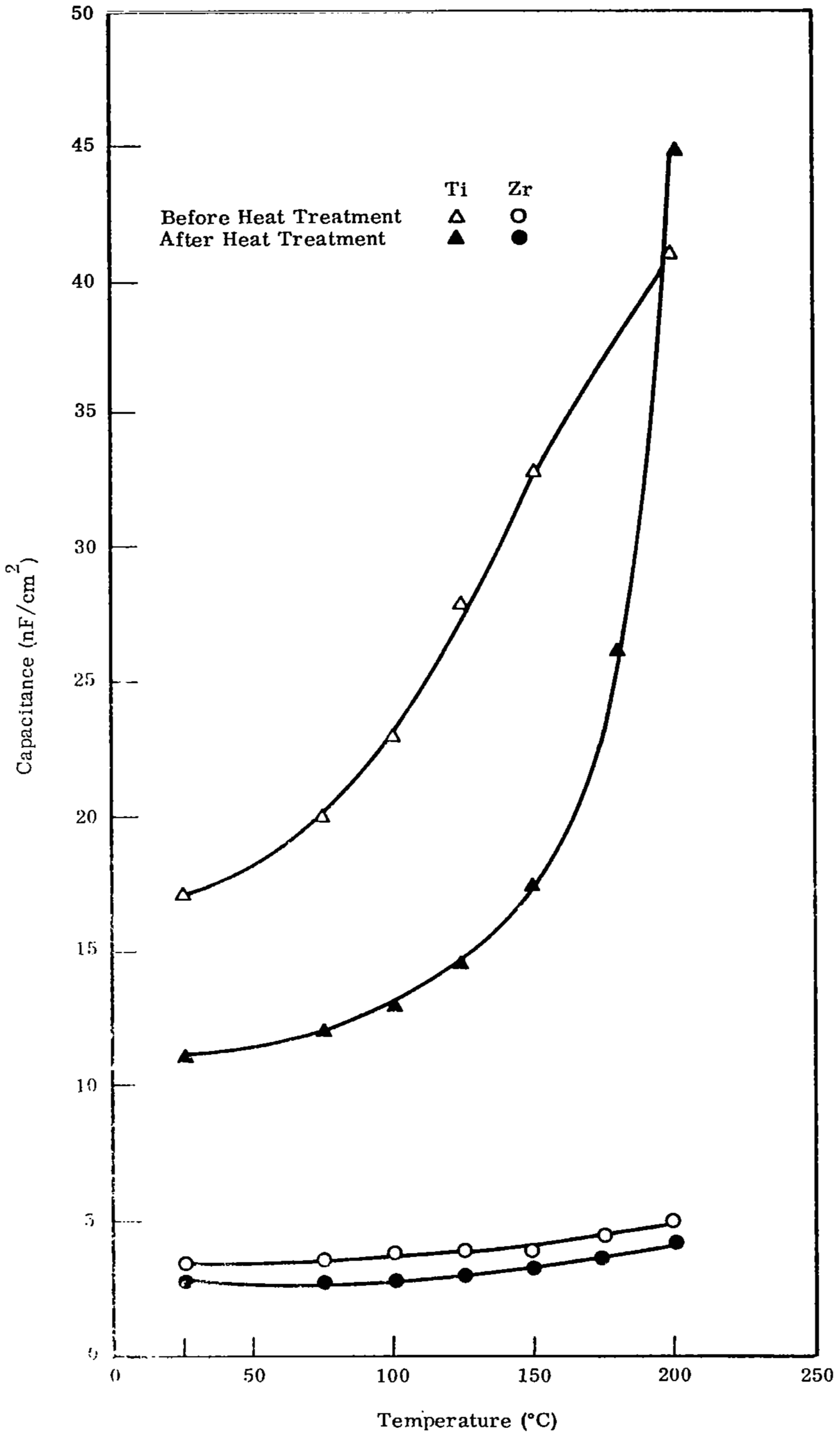

Fig. 2 Temperature-Capacitance Curve for Air Heated Films

4.5.5 Vacuum Heat Treatment

4.5.5.1 General Procedure

Coatings formed at 100 ma/cm^2 on titanium, zirconium, niobium, and tantalum in EDTA baths containing complexed barium, calcium, magnesium, sodium and potassium were given a preliminary capacitance evaluation and then placed in quartz tubes and evacuated to a pressure of 5 μ Hg or less. The tubes were sealed and heated for varying times in a furnace preheated to the desired temperature. The samples were then withdrawn from the furnace, cooled, and opened. They were measured for capacitance and then placed in an air oven at between 200 and 300°C and reoxidized for various time intervals.

4.5.5.1 Results – Coatings on Titanium Substrates

The data obtained from coatings prepared in the above manner on titanium substrates are shown in Table 19. All samples heat treated at 700°C for any length of time were damaged to such a degree that extensive air oxidation did not restore the dielectric properties. The damage is not physical deterioriation of the film but is apparent as high loss factors. Treatment at 600°C was found to be the most satisfactory. The best treatment times used were 15 and 30 min. As the treatment time is extended, healing of the film by air oxidation becomes increasingly difficult.

4.5.5.2 Results – Coatings on Zirconium Substrates

Results of similar heat treatment schedules with zirconium coatings are shown in Table 20. All attempts resulted in either no improvement or very high loss factors. These results are similar to those observed when the coatings on zirconium are air heat treated at these temperatures and indicate that zirconium films respond differently than titanium to heat treatment.

Table 19

HEAT TREATMENT OF COATINGS ON TITANIUM

Sample	EDTA Bath Used	Vacuum Heat Treatment		Initial Capacitance		Capacitance After Heating		Oxidation Treatment		Final Capacitance	
		Temp. (°C)	Time (min)	$C_s^{(1)}$ (nF/cm^2)	Loss D	$C_p^{(2)}$ (nF/cm2)	Loss D	Temp. (°C)	Time (hr)	$C_s^{(1)}$ (nF/cm^2)	Loss D
11-90-A	Calcium	600	15	7.1	0.16	940	2.5	200	1	157	0.26
11-90-B		600	15	9.6	0.18	775	3.7	200	1.5	168	0.18
11-90-C		700	15	7.6	0.165	6,100	9.5	300	2	190(2)	2.1
11-90-D		700	15	8.6	0.14	4,000	12	200	4	1,300(2)	14
11-90-E		700	60	8.3	0.18	2,400	8				
11-90-F		700	60	10.3	0.19	1,500	12.5				
11-92-C	Calcium	600	30	10.8	0.12			300, 200	1.5, 114	100	0.044
11-92-D		600	30	11.7	0.14	175	20	200, 300	16, 1	117(2)	0.22
11-92-E		600	30	7.05	0.11	95	28	200, 300	16, 1	375	0.65
11-92-F		600	30	6.55	0.14			300, 200	1.5, 114	104	0.056
11-94-A	Calcium	600	15	13	0.29	25	0.82				
11-94-B		600	15	15.4	0.28			200	70	117	0.086
11-94-C		600	15	17.1	0.34	21.5	0.95				
11-94-E		600	15	7.35	0.19			200	70	143	0.23
11-94-ER		600	15	20.3	0.27			200	70	118	0.06
11-94-F		600	15	18.5	0.26	8.0	0.38				
11-91-A	Barium	700	60	6.6	0.078	8,500	7	200	1.5	2,250(2)	2
11-91-B		700	60	5.4	0.095	7,750	9.2	200	1	10,000(2)	3.8
11-91-C		600	15	6.4	0.096	575	18	300, 200	1, 15	91	0.088
11-91-D		600	15	8.1	0.11	525	26	200	19	150	0.38
11-93-C	Barium	600	15	17.1	0.36			200	92	120	0.075
11-93-D		600	15	10.8	0.38	(3)		200	92	105	0.09
11-93-E		600	15	1.08	0.25	675	2.2	200	92	36.8	0.5
11-93-F		600	15	5.35	0.35			200	92	94	0.46
11-95-A	Barium	600	15	10.8	0.31	0.35	4.6				
11-95-B		600	15	20.1	0.31			200	70	115	0.08
11-95-C		600	15	17.8	0.30	40(2)	0.95				
11-95-D		600	15	20.8	0.33			200	70	96.5	0.062
11-95-E		600	15	19.8	0.28	8.0	1.1				
11-95-F		600	15	11.2	0.28			200	70	150	0.055

(1) Series capacitance unless noted by (2).
(2) Parallel capacitance unless noted by (1).
(3) Bridge would not null.

Table 20

HEAT TREATMENT OF COATINGS ON ZIRCONIUM

Sample	EDTA Bath Used	Vacuum Heat Treatment		Initial Capacitance		Capacitance After Heating		Oxidation Treatment		Final Capacitance	
		Temp. (°C)	Time (min)	C_s(a) (nF/cm^2)	Loss D	C_p(b) (nF/cm^2)	Loss D	Temp. (°C)	Time (hr)	C_p(b) (nF/cm^2)	Loss D
11-104-A	Barium	600	15	4.65	0.025	62.5	33	200	4.5	0.6(a)	1.8
11-104-B		600	15	3.42	0.028	25	46	200	4.5	0.8(a)	0.76
11-104-E		700	15	2.94	0.025	218	18	200	17	3.5	21
11-104-F		700	15	1.72	0.025	150	31	200	17	25	36
11-104-G		600	15	2.01	0.034		2.2	200, 300	72, 1	(c)	
11-104-H		600	15	2.43	0.036		1.0	200	72	7.5×10^{-3}	3.7
11-104-I		500	30	2.14	0.032	2.40(a)	0.027				
11-105-A	Calcium	500	30	1.59	0.026	1.71(a)	0.03				
11-105-C		700	15	1.54	0.028	3,500	14	200	17	24	12.5
11-105-D		700	15	1.32	0.024	4,000	14.5	200	17	26	15
11-105-E		700	15	2.95	0.030	9,250	8	200, 300	17, 1	22.5	8
11-105-F		700	15	3.4	0.026	250	17	200	17	22.5	16.5
11-105-G		650	15	1.59	0.028	150	10	200, 300	24, 1	4.1(a)	0.077
11-105-H		650	15	2.42	0.032	205	18	200, 300	24, 1	4.3(a)	0.12

(a) Series capacitance unless noted by (b).
(b) Parallel capacitance unless noted by (a).
(c) Bridge would not null.

4.5.5.3 Results – Coatings on Niobium

The types of baths used to produce coatings on niobium were extended to include complexed magnesium, potassium and sodium. The films produced in the last two baths are very white, glassy, and can be formed at lower current densities than those used with the barium, calcium, or magnesium baths. The electrical data are shown in Table 21 for films formed in all the baths.

Treatment at 600°C for 15 min even without subsequent air oxidation produces minimal if any increases in the loss factor while the capacitance is increased by a factor of about 50. Further processing in air reduces the losses to acceptable values and lowers the capacitances to the original values. Processing at 700°C or for any time periods beyond 15 min alters the films so that they cannot be healed by air oxidation.

The best processing technique observed in this data uses films formed in the potassium or magnesium bath and heat treatment at 650°C for 15 min. Films processed under these conditions and healed by air oxidation have shown enhanced electrical properties similar to those observed with titanium coatings.

Time has not permitted a compositional analysis of these coatings. Any extension of this work would logically include further study of the niobium-based coatings. They appear to offer considerable promise at high dielectric films.

4.5.5.4 Results – Coatings on Tantalum

The results using tantalum substrates are shown in Table 22. Attempts were made to form coatings in the sodium and potassium-EDTA baths. However, only very thin interference films were obtained. The magnesium bath did produce coatings similar in appearance to the coatings formed on niobium. However, only slight or no improvement in the capacitance and loss factors was observed when coatings were processed. At best, the capacitance was doubled but at the same time higher loss factors were observed.

Table 21

HEAT TREATMENT OF COATINGS ON NIOBIUM

Sample	EDTA Bath Used	Oxidation Treatment		Initial Capacitance		Capacitance After Heating		Vacuum Heat Treatment		Final Capacitance	
		Temp. (°C)	Time (min)	$C_s^{(1)}$ (nF/cm^2)	Loss D	$C_s^{(1)}$ (nF/cm^2)	Loss D	Temp. (°C)	Time (hr)	$C_s^{(1)}$ (nF/cm^2)	Loss D
11-108-A	Barium	600	15	2.4	0.18	145	0.22	200	104	3.8	0.049
11-108-B		700	30	2.5	0.19	354	0.56	200	99	3.6	0.048
11-108-C		600	15	6.0	0.14	137	0.12	300, 250	1, 17	5.9	0.059
11-108-D		700	60	4.6	0.14	174(2)	5.5	300	41	500(2)	48
11-108-E		600	15	10.4	0.15	122	0.09	200	104	2.45(2)	3.6
11-108-F		700	30	8.9	0.16	144	0.21	200	99	40.5	0.25
11-108-G		600	15	7.0	0.14	98	0.12	300, 250	1, 17	6.6	0.057
11-108-H		700	60	6.0	0.12	127(2)	5.8	300	41	400(2)	30
11-108-I		650	15	5.1	0.14	186	0.78	200	17	52	0.06
11-108-J		650	15	8.8	0.175	2,436	0.70	200	17	59	0.09
11-109-A	Calcium	650	15	2.77	0.17	2.11(2)	30	200	17	1.4(2)	1.7
11-109-B		700	30	2.82	0.18	21(2)	23	200	99	5.6	0.22
11-109-C		650	15	5.9	0.13	130(2)	5.8	200	17	1.8(2)	1.4
11-109-D		650	15	4.2	0.12			200	70	101	0.27
11-109-E		650	15	9.4	0.135			200	70	37.5	0.77
11-109-F		700	30	12.2	0.14	1.2(2)	9.5	200	34	91	0.125
11-109-G		700	60	4.6	0.098	1,000(2)	33	300	41	400(2)	20
11-109-H		700	60	5.3	0.08	7,250(2)	18	300	41	1,400(2)	20
11-109-I		615	15	4.2	0.075			200	70	206	0.54
11-109-J		615	15	6.9	0.12			200	70	75	0.68
11-110-A	Magnesium	650	15	3.2	0.135	200(2)	8.7	200	179	2.45	0.043
11-110-B		600	40	5.5	0.26	1,600(2)	10.5	300	26	(3)	
11-110-D		650	15	8.8	0.26			200	70	169	0.064
11-110-E		700	60	9.8	0.23	7,400(2)	26	300	17	340(2)	17
11-110-F		600	40	14.8	0.21	700(2)	18	200	87	(3)	
11-110-H		650	15	8.3	0.21			200	70	178	0.08
11-110-I		650	15					200	70	5.4	0.045
11-118-C	Potassium	700	40	2.9	0.058	850(2)	32	300	31	1,000(2)	20
11-118-D		650	15	2.7	0.085	240(2)	24	200	109		
11-118-E		650	15	18.9	0.055	210(2)	21	200	109	103	0.07
11-118-F		650	15	11.5	0.069	0.40(2)	40	200	109	136	0.07
11-118-G		650	15	30.2	0.033	(3)		200	109	76	0.16
11-125-B	Sodium	650	15	1.84	0.042	(3)		200	94	3.05	0.18
11-125-C		650	15	1.69	0.04	600(2)	14	200	24	225	0.95
11-125-D		650	15	2.20	0.048			200	70	1.35	0.096
11-125-E		650	15	1.13	0.035			200	70	1.49	0.037
11-125-F		650	15	1.0	0.03			200	70	1.47	0.078
11-125-G		650	15	1.18	0.036			200	70	1.25	0.065

(1) Series capacitance unless noted by (2).
(2) Parallel capacitance unless noted by (1).
(3) Bridge would not null.

Table 22

HEAT TREATMENT OF COATINGS ON TANTALUM

Sample	EDTA Bath Used	Vacuum Heat Treatment		Initial Capacitance		Capacitance After Heat Treatment		Oxidation Treatment		Final Capacitance	
		Temp. (°C)	Time (min)	$C_s^{(1)}$ (nF/cm^2)	Loss D	$C_p^{(2)}$ (nF/cm^2)	Loss D	Temp. (°C)	Time (hr)	$C^{(1)}$ (nF/cm^2)	Loss D
11-112-A	Barium	700	30	4.15	0.048	5.4(1)	0.21	300,200	24,65	4.53	0.048
-B	Barium	700	30	3.78	0.048	5.4(1)	0.165	300,200	24,65	4.58	0.05
-C	Barium	600	40	5.15	0.053	1.5	7.2	200	82	9.05	0.076
-D	Barium	600	40	7.48	0.062	2.0	8.3	200	82	10.1	0.09
-E	Barium	700	60	10.8	0.042	34.5	29	300	46	21.5(2)	2.5
-F	Barium	700	60	13.7	0.031	(3)		300	46	20.1(2)	1.7
-G	Barium	650	15	7.35	0.058	(3)		200	17	0.06(2)	3.3
-H	Barium	650	15	6.75	0.064	(3)		200	17	11.0	0.12
-I	Barium			7.70	0.060						
-J	Barium			6.85	0.059						
11-113-A	Calcium	650	15	5.40	0.054	10.8	0.28	200	17	8.85	0.115
-B	Calcium	650	15	5.65	0.060	11.4(1)	0.26	200	17	7.85	0.105
-C	Calcium			8.45	0.053						
-D	Calcium			9.75	0.054						
-E	Calcium	700	60	16.7	0.053	(3)		300	41	0.1	20
-F	Calcium	700	60	15.7	0.065	(3)		300	41	4.8(2)	2.5
-G	Calcium			14.4	0.046						
-H	Calcium			12.7	0.11						
-I	Calcium			10.3	0.049						
-J	Calcium			9.30	0.048						
11-114-A	Magnesium			3.93	0.16						
-B	Magnesium			3.73	0.16						
-C	Magnesium			8.85	0.12						
-D	Magnesium			8.35	0.135						
-E	Magnesium	700	60	10.0	0.085	(3)		200,300	65,63	(3)	
-F	Magnesium	700	60	16.4	0.18	(3)		200,300	65,63	2,100	14
-G	Magnesium	650	15	9.35	0.115	31.4	5.6	200	17	20.1	0.25
-H	Magnesium	650	15	8.35	0.13	29.4	3.6	200	179	16.9	0.14
-I	Magnesium			11.7	0.12						
-J	Magnesium			9.55	0.125						

(1) Series capacitance unless noted by (2).
(2) Parallel capacitance unless noted by (1).
(3) Bridge would not null.

4.5.5.5 Conclusions — Vacuum Heat Treatment

Vacuum heat treatment of coatings formed on titanium and niobium produces a low resistance film which, when reoxidized, becomes a dielectric with enhanced capacitance and lower losses than observed with the as-produced films. Using the best values observed, some apparent dielectric constants have been calculated (Table 23).

Table 23

APPARENT DIELECTRIC CONSTANTS

Sample	Substrate	EDTA Bath	ϵ As-Produced	ϵ Fired & Oxidized
11-92-F	Titanium	Calcium	160	1,600
11-93-F	Titanium	Barium	120	1,900
11-94-F	Titanium	Calcium	160	760
11-95-F	Titanium	Barium	95	1,300
11-110-D	Niobium	Magnesium	100	1,900
11-118-F	Niobium	Potassium	58	690

These values show that a high dielectric thin film can be produced by use of the techniques described. The vacuum heating and reoxidation healing steps produce an order-of-magnitude improvement for titanium- and niobium-based films.

4.5.5.6 Temperature — Capacitance Measurements

The capacitance and loss as a function of temperature are shown in Fig. 3 for titanium-based films. The effect of sample thickness is also indicated. There is no indication of a Curie point in the temperature range associated with the $BaTiO_3$ Curie point. However, the improvement in capacitance and loss is obvious. Further studies would include measurement of the capacitance at smaller temperature intervals. The thinnest sample, 11-111K, shows high losses and does not react to heat treatment

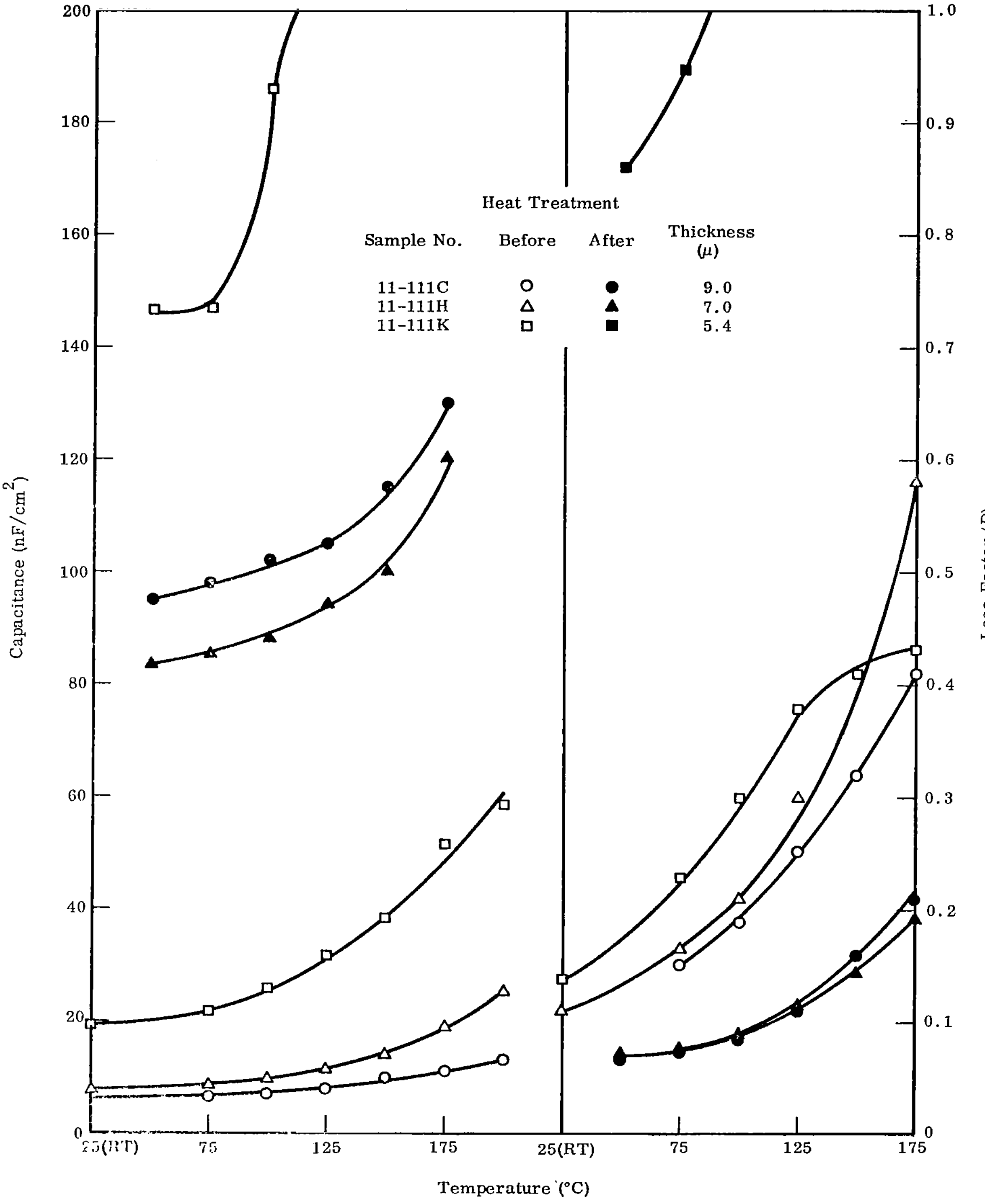

Fig. 3 Capacitance-Temperature Characteristics for Ti-Based Films

in the same way the thicker samples do. Other workers preparing thin films of $BaTiO_3$ by vacuum evaporation techniques have reported that if the crystallite sizes are large even in films between 1 and 2 μ thick, the peak height at the Curie temperature increases and is shifted toward higher temperatures. Conversely, as the crystallite size is reduced, the peak disappears and the temperature curve is flat. Wainer (Ref. 10) and others (Ref. 19) have reported similar results. Therefore, the apparent crystallite size in the films produced here must be very small and electrical characteristics of the TiO_2 mask out much of the transition characteristics that occur at the Curie temperature of this material. The alternate explanation of these results assumes that a structure has been formed that exhibits a high dielectric strength but is not $BaTiO_3$.

4.5.5.7 DC Resistance of Films

The DC resistance of films before and after heat treatment is shown in Table 24. The resistance is lowered markedly by the heat treatment. However, it should be pointed out that even 1 mV produces a field of about 50 V/cm on the 5 μ thick sample. Thus, even though the voltages are small, the field is quite high.

Table 24

DC RESISTANCE OF AS-PRODUCED AND VACUUM HEAT TREATED FILMS

Sample	11-111-C		11-111-H		11-111-K	
	(V)	$(R\Omega)$	(V)	$(R\Omega)$	(V)	$(R\Omega)$
As Produced	0.48	4.8×10^9	0.44	0.44×10^{10}	6.9×10^{-2}	6.9×10^8
	0.76	7.6×10^8	0.90	0.9×10^9	0.23	2.3×10^8
	1.15	1.15×10^8	1.5	1.5×10^8	0.46	0.46×10^8
	2.00	2.0×10^7	2.85	2.85×10^7	0.68	0.68×10^7
	3.5	3.5×10^6	5.2	5.2×10^6	1.0	1×10^6
	5.8	5.8×10^5	9.7	9.7×10^5	1.5	1.5×10^5
Heat Treated	9.0×10^{-4}	9×10^5	6×10^{-4}	6×10^5	4×10^{-3}	4×10^4
	9.7×10^{-4}	9.7×10^5	6.8×10^{-3}	6.8×10^5	6.5×10^{-3}	6.5×10^3
	9.5×10^{-2}	9.5×10^5	6.6×10^{-2}	6.6×10^5	6.5×10^{-2}	6.5×10^3
	0.42	4.2×10^5	0.28	2.8×10^5		
	0.81	8.1×10^4	0.66	6.6×10^4		

4.5.5.8 Frequency Capacitance Characteristics

The effect of vacuum heat treatment on the frequency characteristics is shown in Fig. 4. The heat-treated films possess a steeper slope, and the steep rise of the loss factor has been shifted to lower frequencies. At frequencies above 10,000, the loss factors are virtually the same for all samples.

4.5.5.9 Wet Capacitance

The wet capacitance of the films, both fired and unfired, is shown in Table 25. Phosphoric acid solutions of three different concentrations were used. The data are given in terms of capacitance only, since the area wet by solution could not be measured. The improvement in capacitance due to heat treatment is reflected in the data.

Table 25

WET CAPACITANCE AND LOSS – EDTA FILMS

Sample	40 ml H_2O	75 ml H_2O	85 ml H_2O
As Produced	35 ml H_3PO_4	14 ml H_3PO_4	7 ml H_3PO_4
11-111-C	3 μF	3.2 μF	3.6 μF
	0.67	0.84	1.0
11-111-H	10.7 μF	7 μF	11.8 μF
	0.39	0.58	0.96
11-111-K	6.5 μF	10.4 μF	12.8 μF
	0.52	0.77	1.2
Fired			
11-111-C		20 μF	
		0.7	
11-111-H		17 μF	
		0.58	
11-111-K		16 μF	
		0.68	

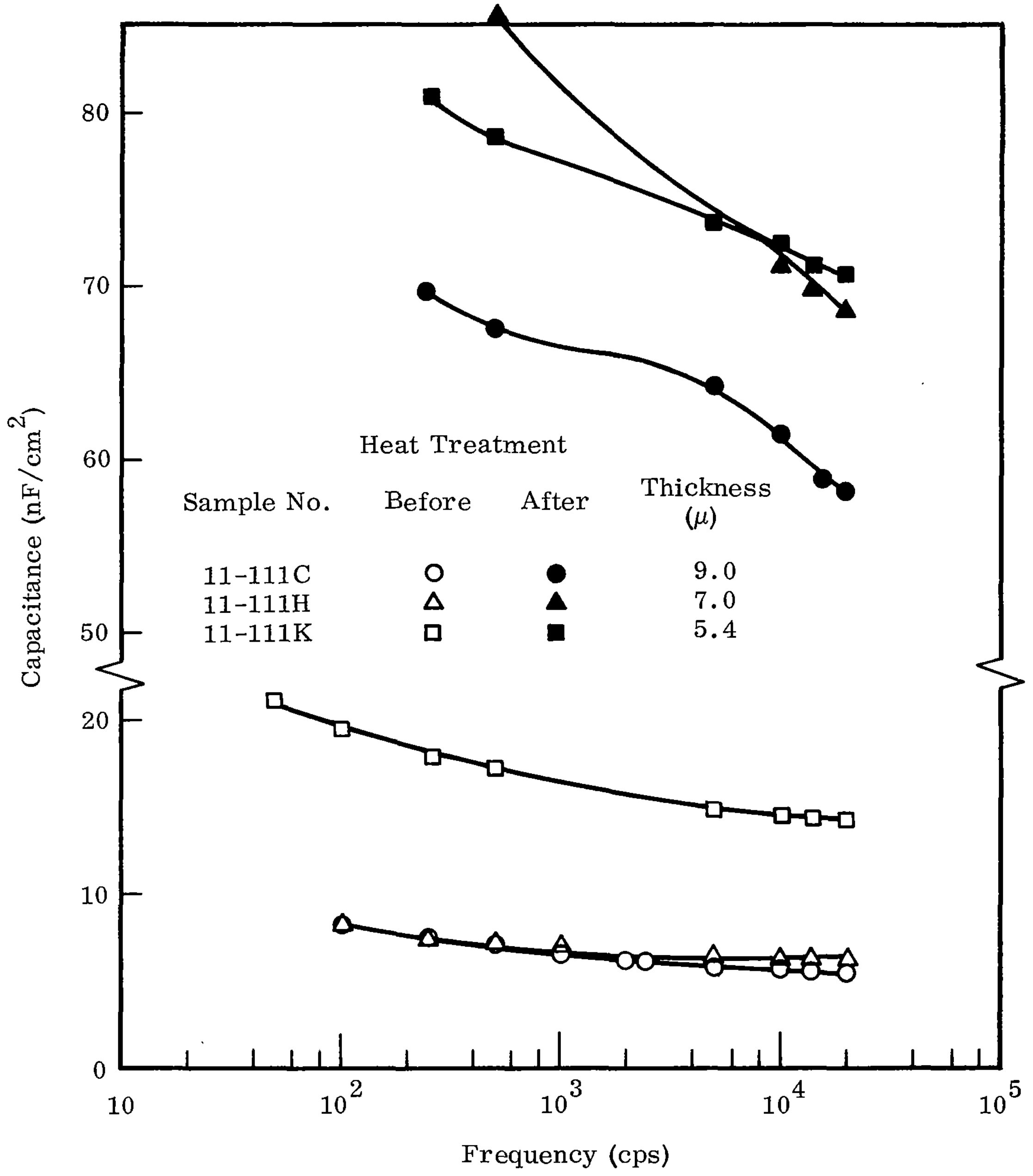

Fig. 4 Capacitance-Frequency Relationships for Vacuum Heat Treated Films

Section 5

CONCLUSIONS AND RECOMMENDATIONS

The vacuum heat treatment of coatings formed on titanium and niobium in EDTA baths containing barium or calcium and magnesium or potassium, respectively, improves the electrical properties of the film by enhancing the apparent dielectric constant to values of about 1000, and by reducing the loss factor. These coatings have been shown to contain up to spectrographically-major amounts of barium. Coatings formed on zirconium and tantalum do not exhibit the same improvements.

Other techniques for depositing high dielectric material have not produced coatings of comparable strength even though the deposition or incorporation of material of high dielectric strength was achieved.

It is recommended that the program be continued and that it should be restricted to a study of coatings formed on titanium and niobium in EDTA baths containing complexed barium and/or calcium and magnesium and/or potassium. The study should include analytical determination of film composition and crystallinity as it is influenced by the process parameters of both as-produced and vacuum heat-treated coatings. A second portion of this study should investigate methods and areas of utilizing films with the determined electrical characteristics. This latter study would include a complete electrical evaluation of the coatings.

Section 6

REFERENCES

1. Lockheed Missiles & Space Company, Electrolytic Preparation of High Dielectric Thin Films, Annual Report for Period 27 Jun 1963 Through 27 Jun 1964, by A. E. Hultquist and M. E. Sibert, TR 4-55-64-1, Sunnyvale, Calif., 1964
2. Landolt-Bornstein, Zahlenwerte and Funktionen aus Physik-Chemie, Astronomie, Geophysik und Technik, Sechste Auflage, II Bond 6. Teil. Berlin, Gottingen-Heidelberg, Springer-Verlag, 1959, pp. 452–494
3. S. Nagasawa, "Dielectric Properties of Oxides of Rare Metals," J. Electrochem. Soc. Japan, Vol. 18, No. 158, 1950
4. B. T. Matthias, Lanthanum Gallate and Lanthanum Aluminate In Ferroelectric Devices, U.S. Patent 2,691,738, 12 Oct 1954
5. -----, "New Ferroelectric Crystals," Phys. Rev., Vol. 75, No. 1771, 1949
6. E. J. W. Verwey, "Controlled-Valency Semiconductors," Phillips Res. Rep., Vol. 5, pp. 173–187, 1950
7. E. J. W. Verwey and R. D. Bugel, Ceramic Materials With a High Dielectric Constant, Phillips Tech. Rev., Vol. 10, p. 231, 1949
8. W. Rath, "Ceramic Insulators for High Frequency Capacitors," Ber. deut keram Ges. u Ver. deut Emailfachleute, Vol. 28, No. 4, 1951, p. 177; see Ceram. Abstracts, Vol. 9, p. 159, 1951
9. H. Stetson and B. Schwartz, J. Am. Ceram. Soc., Vol. 44, pp. 420-1, 1961
10. E. Wainer, Method of Making Ceramic Dielectric, U.S. Patent 2,948,628, 9 Aug 1960
11. S. S. Flascher, "An Aqueous Synthesis of Barium Titanate," J. Am. Chem. Soc., Vol. 77, p. 6194, 1955

12. Massachusetts Institute of Technology, Laboratory for Insulation Research, by A. R. von Hippel, Progress Report No. XXX, Jan 1962, pp. 7–8, 66–77

13. Lockheed Missiles & Space Company, Electrolytic Preparation of High Dielectric Thin Films, Quarterly Report for Period 3 Aug 1964 to 3 Nov 1964, by A. E. Hultquist and M. E. Sibert, Sunnyvale, Calif., 1964

14. -----, Electrolytic Preparation of High Dielectric Thin Films, Quarterly Report for Period 4 Nov 1964 to 3 Feb 1965, by A. E. Hultquist and M. E. Sibert, LMSC-A034389, Sunnyvale, Calif., 1965

15. C. S. Smithells, Metals Reference Book, Vol. I, Third Edition, Washington, D.C., Butterworths, 1962

16. Lockheed Missiles & Space Company, Electrochemical Conversion Coatings on Aluminum," Summary Report for Period 28 Sep 1963 to 28 Sep 1964, Sunnyvale, Calif., 1964

17. R. D. Wales, "The Anodic Formation of Germanium Oxidic Films," J. Electrochem. Soc., Vol. 110, p. 914, 1963

18. C. Feldman, Rev. Sci. Instr., Vol. 26, pp. 463-6, 1955

19. Anliker, Brugger, and Koenzig, Helv. Phys. Acta., Vol. 27, p. 99, 1954

20. French Patent 985,358, 18 Jul 1951

21. C. K. Gravely, Canadian Patent 519,170, 6 Dec 1955

22. K. Traub, C. A. Best, and W. J. Baldwin, Ceram. Age, Vol. 65, No. 1, Jan 1955, pp. 9–14

23. L. Egerton and S. Eloise Koonce, J. Am. Ceramic Soc., Vol. 38, pp. 412–418, 1955

NASA-Langley, 1966 CR-364