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ELECTROLYTIC PREPARATION OF HIGH DIELECTRIC THIN FILMS

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FOREWORD

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

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ABSTRACT

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The second quarterly report on the preparation of high dielectric films by electrolytic techniques is concerned with film preparation and some properties of the films. It has been shown that the EDTA bath is a useful technique for incorporating alkali metal atoms in an anodic film on titanium. There is some indication that a heat treatment of the film will provide an increased dielectric strength.

The hydrolyzed isopropyl titanate bath has been shown to produce a crystalline titania under appropriate conditions. However, cohesion and adhesion of the titania to any substrate is not yet entirely satisfactory.

The KOH-$BaTiO_3$ bath does definitely deposit $BaTiO_3$ in the anodic film. However, due to the complex nature of this film, the electrical characteristics are other than desired and the film is quite sensitive to moisture.

author

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Section 1

INTRODUCTION

The objective of this investigation is the preparation of high dielectric materials in thin film form on refractory metal substrates. Work performed during this quarter has been directed to forming titanate or zirconate films in aqueous and quasi-organic electrolytes. Aqueous and quasi-organic baths used for film formation on titanium substrates include the following: (1) barium acetate - EDTA, (2) lead acetate - EDTA, (3) calcium acetate - EDTA, (4) barium hydroxide-$BaTiO_3$, (5) potassium hydroxide-$BaTiO_3$, (6) potassium silicate-$BaTiO_3$, and (7) isopropyl alcohol-isopropyl titanate with additions of tetraethylammonium hydroxide and $Ba(OH)_2$ or $Ba(OCH_3)_2$. The only bath used in conjunction with the zirconium substrate was the calcium acetate - EDTA bath. Evaluation of these films has been primarily by the comparison of capacitance values using a carbon-silver counter electrode. The effect of temperature, humidity, and heat treatment has also been investigated. Certain films have been submitted for x-ray and semi-quantitative spectrographic analysis.

Section 2

FILM PREPARATION

2.1 GENERAL EXPERIMENTAL PROCEDURE

The procedures used to prepare the baths and the titanium substrates for anodization have been described earlier. (1) The polishing solution used for zirconium substrates contains 10 g. ammonium bifluoride, 40 ml. conc. HNO_3, 20 ml. of 31% H_2SiF_6, and 100 ml. H_2O. The solution is very reactive and must be used carefully to obtain the best results. Satisfactory results can be obtained if the treatment times are between 30 and 60 seconds. Also, the polish temperature should be between 30 and 40°C. The capacitances measured are not affected by the pretreatment to any great extent. Thus, the conclusions drawn from the results of these experiments are sound and a change in polishing procedure will not affect them.

2.2 OCCLUSION OF PARTICULATE HIGH DIELECTRIC MATERIAL

Further experiments using the technique of occluding particulate matter in and on a titanium anodic film have been directed toward determining the bath conditions necessary for formation of a continuous, coherent, and adherent film. It had earlier been reported (1) that a bath consisting of 200 g. of $BaTiO_3$ slurried in a bath containing 100 g./liter KOH produced coatings which were gray-white in appearance.

The results of this quarter's experiments are shown in Table 1. The best range of KOH concentrations was between 50 and 100 g./liter. Concentrations greater or less than this range produce only translucent films or result in complete disintegration of the electrode.

Table 1

CONDITIONS USED IN THE PREPARATION OF
FILMS CONTAINING HIGH DIELECTRIC MATERIAL

Bath Composition g./liter		Anodization Parameters				
KOH	$BaTiO_3$	Temp. °C	Final Voltage	Time Min.	Current Density ma/cm^2	Results
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 g./liter $BaTiO_3$ using different basic salts were used, one 30 g./liter $Ba(OH)_2$ and the other 300 g./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 microns. The hydrolysis of isopropyl titanate in the presence of barium and hydroxyl ions reportedly results in a finer particle size $BaTiO_3$. (2) Some of the precipitate from such a hydrolysis has been used in a 75 g./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 $BaTiO_3$. Some preliminary measurements described in the next section also indicate that the films are different in basic properties.

2.3 PREPARATION OF FILMS IN A HYDROLYZED ISOPROPYL TITANATE BATH

The unique features of the hydrolyzed isopropyl titanate bath have been given in the First Quarterly Report. (1) During this period the bath has been used in attempts to deposit titania or barium titanate in actively growing anodic films. A summary of the conditions and baths used are found in Table 2. The isopropyl titanate was technical grade and was obtained from the DuPont Company. The tetraethylammonium hydroxide was also technical grade, 10% by weight, in a H_2O solution obtained from Eastman Organic Chemicals. Substrates used included titanium, lead, cadmium, and platinum.

Table 2

PREPARATION OF FILMS IN HYDROLYZED ISOPROPYL TITANATE BATHS

Bath Composition g./ml.				Anodizing Conditions		
Isopropyl Titanate	Tetraethyl-Ammonium Hydroxide	$Ba(OCH_3)_2$	$Ba(OH)_2 .8 H_2O$	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

The types of films formed can be generalized for all the 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 drys 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.

2.4 PREPARATION OF FILMS CONTAINING ALKALI METAL OXIDES

The bath developed to codeposit alkali metal atoms in growing anodic films has been used to prepare several series of samples which have been used for film characterization. A detailed study of film composition and properties and their relation to film formation parameters has not been made and will only be made if the dielectric properties of the films are of sufficient potential interest. The range of conditions and bath compositions employed are shown in Table 3. Titanium and titanium alloy substrates have been utilized with barium acetate and calcium acetate baths. Zirconium substrates have been used only with the calcium acetate baths.

Table 3

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

Bath Composition g./l.				Anodizing Conditions			
Barium Acetate	EDTA	H_3BO_3	KOH	Time Min.	Temp. °C	Current Density ma/cm^2	Final Voltage
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
Lead Acetate							
21.5	43	0-7.15	0-28.6	8-22	25-60	50-100	50-170

A visual inspection of all films formed resulted in the following observations for the various substrates used.

- Films formed on titanium in barium acetate baths were gray to light gray in color, adherent, and uniform: in calcium acetate baths they were gray with small white areas and adherent; in lead acetate baths the films were slightly milky brown to translucent. The lead acetate bath is not satisfactory because lead deposition at the cathode depletes the solution. Thus, reproducibility of the anodic coatings is very poor.

- Films formed on zirconium in calcium acetate baths are gray to white, adherent and uniform.

Section 3

PROPERTIES OF FILMS

3.1 INTRODUCTION

The film properties selected for measurement were chemical constitution by spectrographic or x-ray analysis, capacitance at room temperature and room humidity, capacitance in a dry atmosphere, capacitance versus temperature and surface conductance as indicated by the insensitivity of capacitance to counter electrode area. These measurements should indicate the presence of high dielectric material in the films and their effect, if any, on the electrical properties. Additional measurements at 1 megacycle and inert wet capacitance values are not determined unless films exhibit the desired high dielectric properties.

3.2 SPECTROGRAPHIC ANALYSIS

Films formed on titanium in the EDTA-barium acetate bath and the KOH-$BaTiO_3$ bath have been analyzed semiquantitatively for the metal atom constituents. The results are shown in Table 4. The films were stripped from the titanium substrate by the bromine-methanol method. The aluminum, magnesium, and silicon are at least, in part, impurities in the metal substrate. The boron is a contaminant from the boric acid in the EDTA while the iron is contributed by the $BaTiO_3$. Both samples indicated major amounts (greater than 10%) for barium and titanium. The EDTA bath definitely can deposit alkali metal atoms in a growing titanium oxide film.

Table 4

SPECTROGRAPHIC ANALYSIS OF TITANIUM FILMS

Sample No.	Bath Type	CONSTITUENTS FOUND Major Greater than 10%	Minor Greater than 1% but less than 10%	Trace Less than 1%
11-29-E	$KOH \cdot BaTiO_3$	Ti, Ba	Si	Al, Mg, Fe
11-27-E	$Ba(C_2H_3O_2)_2 \cdot EDTA$	Ti, Ba	Si	Al, Mg, B

3.3 X-RAY ANALYSIS

Analysis by x-ray techniques should provide some indication of the crystallinity of the sample films. Except for the one formed in the EDTA bath, the films were stripped again in bromine-methanol and ground to a powder in an agate mortar and pestle. The analytical results are shown in Table 5. The only lines observed

Table 5

X-RAY ANALYSIS OF TITANIUM FILMS

Sample No.	Bath Type	Observed Lines d.	Observed Lines I/I_o	Known $BaTiO_3$ Lines d.	Known $BaTiO_3$ Lines I/I_o	TiO_2 Rutile d.	TiO_2 Rutile I/I_o	TiO_2 Anatase d.	TiO_2 Anatase I/I_o
11-15A	$KOH \cdot BaTiO_3$	2.85	100	2.84	100				
		2.83		2.82					
43-7	Hydrolyzed Isopropyl Titanate	3.52	100			3.25	100	3.51	100
		3.26	58			1.69	50	1.89	33
		2.49	35			2.49	41	2.38	22
		2.36	24			2.19	22	1.69	21
		2.19	18.5			1.62	16	1.66	19
		1.90	47			1.36	16	1.48	13
		1.69	70					1.26	10
		1.67	35						
		1.63	18						
						Ti Metal d.	I/I_o		
11-25A	$Ba(C_2H_3O_2)_2 \cdot EDTA$	3.22	22						
		2.35	70			2.24	100		
		2.26	100			2.56	30		
		2.03	84			2.34	26		

in the film formed in $KOH \cdot BaTiO_3$ are the most intense lines for $BaTiO_3$. Thus, it is concluded that the technique of anodizing in a basic bath containing suspended $BaTiO_3$ will form a film containing enough $BaTiO_3$ to be detected by x-rays.

The results of x-ray analysis for the hydrolysis film indicates both anatase and rutile to be present. Since no barium was present in this bath, barium titanate was not expected. These results are of interest because the temperature of formation of this film was only room temperature. Normally, an amorphous oxide would be expected from such a hydrolysis performed in neutral or acid solutions. In basic solutions there is less tendency for hydration to occur. (3) Another explanation for this crystallinity may be the high fields experienced by the film during deposition. When hydrolysis is carried out using a platinum anode and only a small field is employed, the film is amorphous in structure. The effect of high fields in promoting the crystallization of anodic films has been observed by many others. (4)

The film formed in the EDTA-barium acetate bath was not stripped prior to x-ray analysis. Thus, the lines due to the metal substrate are present. The only line not attributable to the metal is the 3.22 line which was weak and is probably due to some rutile developed in the film during heat treatment. Some interesting electrical measurements described in Section 4 indicate the presence of a higher dielectric material than is normally observed with amorphous titania.

3.4 CAPACITANCE MEASUREMENTS

The capacitance measurements using Ag-Aquadag counter electrodes have been made on all samples whose films were adherent and uniform. The results in Table 6 are specific values obtained when measured 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 respective baths.

The results indicate that the films formed in the $KOH \cdot BaTiO_3$ bath are very moisture sensitive. The hydrolyzed isopropyl titanate films are also probably moisture sensitive. However, the films formed in the EDTA bath are not and exhibit only slight changes in capacitance due to moisture. In all samples the dissipation is lowered by the same relative amount as the capacitance when mositure is removed from the films.

The possibility of forming conductive surface coatings is always present in the basic baths employed. The technique employed to determine if the films are conducting is simply to measure the capacitance with two sizes of counter electrodes. If the film is conducting, the same capacitance should be measured by both electrodes. If the capacitance values vary directly with the area of the electrodes, then the film is non-conducting. The large changes in capacitance in the films formed in KOH-$BaTiO_3$ indicated such a measurement should be made. The capacitances measured with two sizes of mercury electrodes are in Table 7. The results show that the coatings are not conductive on the surface. Even the coatings doped with lead are not conductive even though lead dioxide is conductive.

Table 6

ROOM TEMPERATURE CAPACITANCE AT ROOM HUMIDITY AND OVER DRIERITE

Sample No.	Bath Type	Sample Thickness Microns	Capacitance ($\mu f/cm^2$)	
			In Air	Over Drierite
11-29A	KOH-$BaTiO_3$	67	0.50	1.9×10^{-4}
43-12A	Hydrolyzed Isopropyl Titanate	Not measured	0.019	Not measured
		Not measured	0.044	0.022
11-25E	$Ba(C_2H_3O_2)_2 \cdot$EDTA	10	0.079	Not measured
11-27D	$Ba(C_2H_3O_2)_2$.EDTA	26	0.074	0.049
11-27C	$Ba(C_2H_3O_2)_2 \cdot$EDTA	24	0.0495	0.048

Several attempts have been made to measure the capacitance as a function of temperature. This measurement is important in that all the high dielectric

Table 7

CAPACITANCES MEASURED WITH TWO Hg ELECTRODES

		Capacitance µf/cm^2			
Sample No.	Bath Type	Large Electrode	Small Electrode	Ratio C_e/C_s	Ratio of Electrode Areas
11-29A	KOH-BaTiO$_3$	0.208	0.057	3.65	4.6
11-32B	$Pb(C_2H_3O_2)_2$·EDTA	0.038	0.013	2.9	4.6
11-33A	$Pb(C_2H_3O_2)_2$·EDTA	0.006	0.00097	6.2	4.6
11-33B	$Pb(C_2H_3O_2)_2$·EDTA	0.0042	0.0012	3.5	4.6

materials exhibit a sudden rise in capacitance at the temperature (the Curie temperature) where a change in crystal structure occurs. The data are shown in Table 8.

Table 8

CAPACITANCE TEMPERATURE RELATIONSHIP

Sample No.	Bath Type	Temp. °C	C_s (µf/cm^2)
11-40S	KOH-BaTiO$_3$ (from hydrolysis of Isopropyl Titanate)	25	Results very erratic. Dissipation factor very high ~ 20.
		65	
		100	
		120	
		190	
11-29C	KOH-BaTiO$_3$ (Commercial BaTiO$_3$ from TAM)	25	0.390
		50	0.0013
		70	0.0018
		95	0.0024
		110	0.0032
		120	0.0019
		150	0.0018
11-27C	$Ba(C_2H_3O_2)_2$·EDTA	76	0.0043
		88	0.0044
		90	0.0049
		115	0.0046
		148	0.0049
11-33A	$Pb(C_2H_3O_2)_2$·EDTA	26	0.0215
		85	0.020
		120	0.022
		150	0.027

The above results show very little indication for the presence of a high dielectric material except for the film 11-29C. The capacitance of this film approximately doubled while being heated from 50° to 110°C, and a maximum was observed at that temperature. Since this film is actually a composite of $BaTiO_3$ crystals in an amorphous TiO_2 and K_2O material, it is possible that the maximum was shifted to a lower temperature. There is also the possibility of a systematic error in the apparatus used. The apparent influence of moisture is seen by the sharp reduction in capacitance on increasing the temperature from 25 to 50°C.

A series of heat treatments were given to films prepared in the barium acetate-EDTA bath. The object of these treatments was to promote the crystallization of the film. The pertinent data are shown in Table 9. All treatments were performed in air. The titanium metal not covered by the coating is oxidized readily at these temperatures. The obvious conclusion here is that heat treatment does cause an increase in capacitance. Whether it is due to crystallization of the film has not been conclusively demonstrated. Additional heat treatment at 800°C in air results in catastrophic oxidation of the titanium metal. The results are sufficiently encouraging to justify further work on heat treatment of these films.

Table 9

HEAT TREATMENT OF BARIUM ACETATE-EDTA FILMS

	Heat Treatment			Thickness- μ		
Sample No.	Time Min.	Temp. °C	C_s $\mu f/cm^2$	Dermitron	Micrometer	Dielectric Constant
11-24E	None		7.85×10^{-3}	10	10	89
11-24D	30	260	5.52×10^{-3}	17		106
11-24A	60	260	11.3×10^{-3}	12		152
11-24C	120	260	80.8×10^{-3}	5		456
11-24B	70	290	25.4×10^{-3}	11		314

Section 4

FUTURE WORK PLANS

A contract review meeting with Mr. J. Gangler of NASA Headquarters was held on 4 January 1965. At this meeting it was agreed that the work on the barium titanate films should be phased out and work on tantalates, niobates, and zirconates should be emphasized during the remaining contract period. Thus, during the next quarter only a limited amount of work will be done on barium titanate films. This will be concerned with heat treatment studies, and some improved analyses of the films. The study on the preparation of high dielectric zirconates will be completed. Application of previously developed and proposed alternate techniques to the preparation of high dielectric niobates and tantalates will be initiated. The experimental program will include work on aqueous systems, molten salt systems, and deposition from the vapor phase.

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