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QUARTERLY REPORT

For Period

May 4, 1965 to August 3, 1965

N65-33872

FACILITY FORM 602

(ACCESSION NUMBER) 12 (PAGES) CR 67613 (NASA CR OR TMX OR AD NUMBER)

(THRU) 1 (CODE) 17 (CATEGORY)

ELECTROLYTIC PREPARATION OF HIGH DIELECTRIC FILMS

GPO PRICE $ _____

CSFTI PRICE(S) $ _____

Hard copy (HC) 1.00

Microfiche (MF) .50

ff 653 July 65

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Work carried out under Contract NASw-969
for
Office of Advanced Research & Technology
NASA Headquarters, Washington 25, D.C.

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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 by electrochemical techniques. Work performed during this quarter has been directed toward improving the capacitance of titanate, zirconate, niobate and tantalate films by vacuum heat treatment. The baths used have been of the EDTA type previously described and have used Group IIA and IA cations as complexed potential film modifiers. Reoxidation of the reduced films (produced in the vacuum heat treatment) by heating in air restores the insulative nature of the films, and in certain cases, a film with a lower loss and a higher capacity than the original films is produced.

This quarterly report is concerned only with the results of the vacuum heat treatment in terms of electrical measurements of capacitance and loss factors. The final report will contain additional information concerning the electrical properties as well as information concerning the composition and crystallinity of the coatings.

Section 2

HEAT TREATMENT OF COATINGS

2.1 INTRODUCTION

Repeated spectrographic examination of films formed on titanium, zirconium, and niobium under certain conditions in a bath containing an EDTA complex of barium or calcium have shown the presence of barium or calcium. However, the electrical properties of these films indicated a lack of crystallinity of the type that is associated with a high dielectric material. Attempts were made to induce the formation of a crystalline material by heating the films in air. Although the results were encouraging, oxidation of the substrate limited the temperatures at which the films could be processed. Thus a series of experiments were performed in which the films were heated in a vacuum and then reoxidized to eliminate film conductivity. The time and temperature of processing are the important factors in determining the final capacity of the films.

2.2 GENERAL PROCEDURE

Films have been formed on titanium, zirconium, niobium, and tantalum substrates using EDTA baths containing complexed barium, calcium, magnesium, sodium or potassium. All films have been formed at 100 $ma/_{cm}2$ for five minutes. The formation parameters used have varied only slightly and variations in electrical properties due to these factors are small compared to improvements noted if any.

Films were given a preliminary evaluation, then placed in quartz tubes, pumped until a vacuum of less than 5μ Hg was obtained and then sealed. These samples were placed in a preheated furnace. The samples were removed from the furnace, cooled and then opened. They were then placed in an air oven at between 200 and 300°C and allowed to reoxidize.

2.3 RESULTS OF HEAT TREATMENT

2.3.1 Coatings on Titanium Substrates

The data obtained from coatings prepared and vacuum heat treated on titanium substrates is shown in Table 1. All samples heat treated at 700°C for any length of time were damaged to such a degree that air oxidation did not heal them. The extent of this damage was not visible as physical damage but appears as high loss factors. The treatment at 600°C was found to be the most satisfactory. The best treatment times used were 15 and 30 minutes. As the treatment time is extended, healing of the film by air oxidation becomes increasingly difficult.

2.3.2 Coatings on Zirconium Substrates

Attempts were made to improve the capacitance of films formed on zirconium by vacuum heat treatment. This data is shown in Table 2. All attempts resulted in either no improvement or drastically deteriorated capacitance and loss factors. These results here are in keeping with those observed when air heat treatment is used and indicated that zirconium films respond differently than titanium films.

2.3.3 Coatings on Niobium Substrates

The types of baths used to produce coatings on niobium were extended to include complexed magnesium, potassium, and sodium. The films produced in the latter baths are very white, glassy, and are formed at lower current densities than those used with calcium, barium, or magnesium. The electrical data is shown in Table 3 for these films before and after the vacuum heat treatment.

It should be noted first that treatment at 600°C for 15 minutes without subsequent air oxidation produces minimal if any increases in losses while the capacitance is increased by about a factor of 50. Further processing in air reduces the losses to acceptable values with drastic reduction of the capacitance, to levels about the same as the initial values.

TABLE 1

HEAT TREATMENT OF COATINGS ON TITANIUM

Sample Number	EDTA Bath Used	VACUUM HEAT TREATMENT Temp. °C	Time Min.	INITIAL CAPACITANCE Cs (1) nf/cm²	Loss D	CAPACITANCE AFTER HEATING Cp (2) nf/cm²	Loss D	OXIDATION TREATMENT Temp. °C	Time Hours	FINAL CAPACITANCE Cs (1) nf/cm²	Loss D
11-90-A	Calcium	600	15	7.1	0.16	940	2.5	200	1	157	0.26
B		600	15	9.6	0.18	775	3.7	200	1.5	168	0.18
C		700	15	7.6	0.165	6100	9.5	300	2	190(P)	2.1
D		700	15	8.6	0.14	4000	12	200	4	1200(P)	14
E		700	60	8.3	0.18	2400	8				
F		700	60	10.3	0.19	1500	12.5				
11-92-C	Calcium	600	30	10.8	0.12	--	--	300,000	1.5,114	100	0.044
D		600	30	11.7	0.14	175	20	200,300	16,1	117(P)	0.22
E		600	30	7.05	0.11	95	28	200,300	16,1	375	0.65
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	--	--		
B		600	15	15.4	0.28	--	--	200	70	117	0.086
C		600	15	17.1	0.34	215	0.95	--	--		
E		600	15	7.35	0.19	--	--	200	70	143	0.23
ER		600	15	20.3	0.27	--	--	200	70	118	0.06
F		600	15	18.5	0.26	8.0	0.38	--	--		
11-91-A	Barium	700	60	6.6	0.078	8500	7	200	1.5	2250(P)	
B		700	60	5.4	0.095	7750	9.2	200	1	10,000(P)	3.8
C		600	15	6.4	0.096	575	18	300,200	1, 15	91	0.088
D		600	15	8.1	0.11	525	26	200	19	150	0.38

TABLE 1 - HEAT TREATMENT OF COATINGS ON TITANIUM (Continued)

Sample Number	EDTA Bath Used	VACUUM HEAT TREATMENT Temp. °C	Time Min.	INITIAL CAPACITANCE C_s (1) nf/cm²	Loss D	CAPACITANCE AFTER HEATING C_p (2) nf/cm²	Loss D	OXIDATION TREATMENT Temp. °C	Time Hours	FINAL CAPACITANCE C_s (1) nf/cm²	Loss D
11-93-C	Barium	600	15	17.1	0.36	--		200	92	120	0.075
D		600	15	10.9	0.38	(3)		200	92	105	0.09
E		600	15	1.08	0.25	675	2.2	200	92	36.8	0.5
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				
B		600	15	20.1	0.31			200	70	115	0.08
C		600	15	17.8	0.30	40(S)	0.95				
D		600	15	20.8	0.33			200	70	96.5	0.062
E		600	15	19.8	0.28	8.0	1.1				
F		600	15	11.2	0.28			200	70	150	0.055

(1) Series Capacitance unless noted by (P)

(2) Parallel Capacitance unless noted by (S)

(3) Bridge would not null.

TABLE 2

HEAT TREATMENT OF COATINGS ON ZIRCONIUM

Sample Number	EDTA Bath Used	VACUUM HEAT TREATMENT Temp. °C	Time Min.	INITIAL CAPACITANCE Cs(1) nf/cm²	Loss D	CAPACITANCE AFTER HEATING Cp(2) nf/cm²	Loss D	OXIDATION TREATMENT Temp. °C	Time Hours	FINAL CAPACITANCE Cp(2) nf/cm²	Loss D
11-104-A	Barium	600	15	4.65	0.025	62.5	33	200	4.5	0.6(S)	1.8
B		600	15	3.42	0.028	25	46	200	4.5	0.8(S)	0.76
E		700	15	2.94	0.025	218	18	200	17	3.5	21
F		700	15	1.72	0.025	150	31	200	17	25	36
G		600	15	2.01	0.034		2.2	200,300	72,1	(3)	
H		600	15	2.43	0.036		1.0	200	72	7.5×10^{-3}	3.7
I		500	30	2.14	0.032	2.40(S)	0.027				
11-105-A	Calcium	500	30	1.59	0.026	1.71(S)	0.03				
C		700	15	1.54	0.028	3,500	14	200	17	24	12.5
D		700	15	1.32	0.024	4,000	14.5	200	17	26	15
E		700	15	2.95	0.030	9,250	8	200,300	17,1	22.5	8
F		700	15	3.4	0.026	250	17	200	17	22.5	16.5
G		650	15	1.59	0.028	150	10	200,300	24,1	4.1(S)	0.077
H		650	15	2.42	0.032	205	18	200,300	24,1	4.3(S)	0.12

(1) Series Capacitance unless noted by (P)

(2) Parallel Capacitance unless noted by (S)

(3) Bridge would not null

TABLE 3

HEAT TREATMENT OF COATINGS ON NIOBIUM

Sample Number	EDTA Bath Used	VACUUM HEAT TREATMENT Temp. °C	Time Min.	INITIAL CAPACITANCE Cs(1) nf/cm2	Loss D	CAPACITANCE AFTER HEATING Cs(1) nf/cm2	Loss D	OXIDATION TREATMENT Temp. °C	Time Hours	FINAL CAPACITANCE Cs(1) nf/cm2	Loss D
11-108-A	Barium	600	15	2.4	0.18	145	0.22	200	104	3.8	0.049
B		700	30	2.5	0.19	354	0.56	200	99	3.6	0.048
C		600	15	6.0	0.14	137	0.12	300,250	1,17	5.9	0.059
D		700	60	4.6	0.14	174(P)	5.5	300	41	500(P)	48
E		600	15	10.4	0.15	122	0.09	200	104	2.45(P)	3.6
F		700	30	8.9	0.16	144	0.21	200	99	40.5	0.25
G		600	15	7.0	0.14	98	0.12	300,250	1,17	66	0.057
H		700	60	6.0	0.12	127(P)	5.8	300	41	400(P)	30
I		650	15	5.1	0.14	186	0.78	200	17	52	0.06
J		650	15	8.8	0.115	2430	0.70	200	17	59	0.09
11-109-A	Calcium	650	15	2.77	0.17	2.11(P)	30	200	17	1.4(P)	1.7
B		700	30	2.82	0.18	21(P)	23	200	99	5.6	0.22
C		650	15	5.9	0.13	130(P)	5.8	200	17	1.8(P)	1.4
D		650	15	4.2	0.12	--	--	200	70	101	0.27
E		650	15	9.4	0.135	--	--	200	70	37.5	0.77
F		700	30	12.2	0.14	1.2(P)	9.5	200	34	91	0.125
G		700	60	4.6	0.098	1000(P)	33	300	41	400(P)	20
H		700	60	5.3	0.08	7250(P)	18	300	41	1400(P)	20
I		650	15	4.2	0.075	--	--	200	70	206	0.54
J		650	15	6.9	0.12	--	--	200	70	75	0.68

TABLE 3 - HEAT TREATMENT OF COATINGS ON NIOBIUM (Cont.)

Sample Number	EDTA Bath Used	VACUUM HEAT TREATMENT Temp. °C	Time Min.	INITIAL CAPACITANCE Cs(1) nf/cm²	Loss D	CAPACITANCE AFTER HEATING Cs(1) nf/cm²	Loss D	OXIDATION TREATMENT Temp. °C	Time Hours	FINAL CAPACITANCE Cs(1) nf/cm²	Loss D
11-110-A	Magnesium	650	15	3.2	0.135	200(P)	8.7	200	179	2.45	0.043
B		600	40	5.5	0.26	1600(P)	10.5	300	26	(3)	
D		650	15	8.8	0.26	--	--	200	70	169	0.064
E		700	60	9.8	0.23	7400(P)	26	300	17	340(P)	17
F		600	40	14.8	0.21	700(P)	18	200	87	(3)	
H		650	15	8.3	0.21	--	--	200	70	178	0.08
I		650	15	--	--	--	--	200	70	5.4	0.045
11-118-C	Potassium	700	40	2.9	0.058	850(P)	32	300	31	1000(P)	20
D		650	15	2.7	0.085	240(P)	24	200	109		
E		650	15	18.9	0.055	210(P)	21	200	109	103	0.07
F		650	15	11.5	0.069	0.40(P)	40	200	109	136	0.07
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
C		650	15	1.69	0.04	600(P)	14	200	24	225	0.95
D		650	15	2.20	0.048			200	70	1.35	0.096
E		650	15	1.13	0.035			200	70	1.49	0.037
F		650	15	1.0	0.03			200	70	1.47	0.078
G		650	15	1.18	0.036			200	70	1.25	0.065

(1) Series Capacitance unless noted by (P)

(2) Parallel Capacitance unless noted by (S)

(3) Bridge would not null.

Processing at 700°C or at any temperature for time periods beyond 15 minutes produces films that cannot be healed by the subsequent air oxidation.

The best processing technique observed in this data uses films formed in the potassium or magnesium bath and heat treatments at 650°C for 15 minutes. Films processed by this technique have shown electrical properties similar to the titanium films. This result is not unusual inasmuch as niobium and titanium have quite a few other properties that are similar.

Time has not permitted a compositional analysis of these coatings. An extension of this program would logically include this study as these coatings are quite promising.

2.3.4 Coatings on Tantalum Substrates

The results of processing coatings formed on tantalum in the EDTA baths are shown in Table 4. Attempts were made to form coatings on tantalum in the potassium and sodium EDTA bath. However, only thin interference coatings were obtained. The magnesium-EDTA 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 the coatings were heat treated. At best the capacitance was doubled, but at the same time higher loss factors were observed.

TABLE 4

HEAT TREATMENT OF COATINGS ON TANTALUM

Sample Number	EDTA Bath Used	VACUUM HEAT TREATMENT Temp. °C	Time Min.	INITIAL CAPACITANCE Cs(1) nf/cm2	Loss D	CAPACITANCE AFTER HEATING Cp(2) nf/cm2	Loss D	OXIDATION TREATMENT Temp. °C	Time Hours	FINAL CAPACITANCE Cs(1) nf/cm2	Loss D
11-112-A	Barium	700	30	4.15	0.048	5.4(S)	0.21	300,200	24, 65	4.53	0.048
B		700	30	3.78	0.048	5.4(S)	0.165	300,200	24, 65	4.58	0.05
C		600	40	5.15	0.053	1.5	7.2	200	82	9.05	0.076
D		600	40	7.48	0.002	2.0	8.3	200	82	10.1	0.09
E		700	60	10.8	0.042	34.5	29	300	46	21.5(P)	2.5
F		700	60	13.7	0.031	(3)		300	46	20.1(P)	1.7
G		650	15	7.35	0.058	(3)		200	17	0.06(P)	3.3
H		650	15	6.75	0.064	(3)		200	17	11.0	0.12
11-113-A	Calcium	650	15	5.40	0.054	10.8	0.28	200	17	8.85	0.115
B		650	15	5.65	0.060	11.4(S)	0.26	200	17	7.85	0.105
E		700	60	16.7	0.053	(3)		300	41	0.1	20
F		700	60	15.7	0.065	(3)		300	41	4.8(P)	2.5
11-114-E	Magnesium	700	60	10.0	0.085	(3)		200,300	65, 63	(3)	
F		700	60	16.4	0.18	(3)		200,300	65, 63	2100	14
G		650	15	9.35	0.115	31.4	5.6	200	17	20.1	0.25
H		650	15	9.35	0.13	29.4	3.6	200	179	16.9	0.14

(1) Series Capacity unless noted by (P).

(2) Parallel Capacity unless noted by (S).

(3) Bridge would not null.

Section 3

CONCLUSIONS

Vacuum heat treatment of coatings formed in EDTA baths on titanium and niobium produces a low resistance film. When reoxidized in air at 200 to 300°C the coating becomes a dielectric with enhanced capacitance and lower losses. Using the values of coatings on titanium treated in such a manner, and thickness measurements made by the Dermitron instrument, the apparent dielectric constants have been calculated.

TABLE 5

Apparent Dielectric Constants

Sample Number	Substrate	EDTA Bath	As Formed	Fired & Oxidized
11-92-F	Titanium	Calcium	160	1600
11-93-F	Titanium	Barium	120	1900
11-94-F	Titanium	Calcium	160	760
11-95-F	Titanium	Barium	95	1300
11-110-D	Niobium	Magnesium	99.5	1900
11-118-F	Niobium	Potassium	58	690

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

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