ON THE TECHNOLOGY OF DEPOSITION OF POLYCRYSTALLINE THIN FILMS OF FERRO- AND ANTI-FERROELECTRICS ON METALLIC SUBSTRATES

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Thin $PbZrO_3$, $PbTiO_3$ and $BaTiO_3$ films have been deposited on metallic substrates using the electrophoresis process in uniform electric field.

Mechanical and electrical properties of these films depend on the choice of parameters of the technological process.

Such thin films permit the construction of very small capacitors (dielectric thickness ranging from 0.5 to 180 μm) of big capacity and small dielectric losses. Very good attachment of the deposited film to platinum substrate has been achieved by roasting it at 1350°C or adding small amounts of special bonding agent to the suspension.

Optimal electrophoresis conditions have been determined. It is also described how to obtain thin films with an *a priori* given thickness.

1. Introduction

Thin insulating coatings are usually deposited on metallic substrates using, among others, methods based on the so-called electrokinetic phenomena, *i.e.* electrophoresis, dielectrophoresis and sedimentation.

The present study made use of the electrophoresis processs for the deposition of thin films from materials which exhibit ferroelectric and antiferroelectric properties in certain temperature ranges. Ceramic dielectrics of such type as, *e.g.*, $BaTiO_3$, $PbTiO_3$ and $PbZrO_3$, are characterized by high values of dielectric constant. Thin films from such materials deposited on suitable conducting substrates can be used in the construction of miniature capacitors with high capacity which find various applications in miniature electronic elements. The electrical and mechanical properties of such thin films do not depend on the material alone, they are also highly dependent on the technology of deposition. The present paper gives the results of systematic studies whose aim has been the investigation of the physics in the electrophoresis process. The knowledge of this permitted the determination of conditions in which the films with reproducible ferroelectric properties can be obtained.

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2. *Preparation of materials*

In order to obtain ceramic samples of ferroelectric materials the author has used commonly accepted technological processes for the particular compounds. In case of ceramic $PbTiO_3$ the procedure was based on the data of Glozman [1]. $PbZrO_3$ was obtained according to Glücksman [2] while $BaTiO_3$ according to Jeżewski [3]. Table I shows optimal values of the basic parameters of the technological processes used in the present work.

TABLE I

Basic technological data on the production of ceramic samples

Raw material	Pressure during pressing	Temperature during sintering			Sintering time [h]
		I sample	II sample	III sample	
$PbO+TiO_2 = PbTiO_3$	5000 at	850	1100	1250	3
$PbO+ZrO_2 = PbZrO_3$	5000 at	900	1250	1350	3
$BaCO+TiO_2 = BaTiO_3+CO_2$	5000 at	1100	1200	1350	4

TABLE II

Some properties of ceramic materials used in the present experiment

Material	Density d[g/cm^3]	Porosity p[%]	Dielectric const. ε		Dielectric loss tg δ		T_c[°C]
			20°C	T_c	20°C	T_c	
$PbTiO_3$	6.9	9.7	200	4000	0.025	—	488
$PbZrO_3$	7.45	9.5	350	6800	0.02	0.001	233
$BaTiO_3$	5.2	9.8	1500	12000	0.009	0.009	120

The mean values of the results of measurements of some mechanical and electrical properties of the ceramic materials specified in Table I are summarized in Table II.

The present paper confirmed the strong dependence of the mechanical and electrical properties of ceramic samples on the technology of their preparation found also by other authors. The averaged results of measurements and technological conditions given in Tables I and II are in agreement with the data from literature.

The properties of ferro- and antiferroelectric thin films obtained in the present experiment are in close relation with the properties of the corresponding ceramic raw materials. The results of studies on the technology and properties of thin films given in the following sections concern only one of the series of ceramic samples (see Table I and II).

Ceramic pellets were ground to powder which was used in the preparation of the suspension for the deposition of thin films. Using the method described by Khodakov [4] the following grain size fractions were obtained: less than 1 μm, 1–3 μm, 3–5 μm, 5–7 μm, and 7–10 μm.

3. *Technology of deposition of thin films*

The deposition of different dielectric materials by means of electrophoresis requires completely different technological conditions. The particular difficulty encountered in the present work was the formation of thin films with repeatable dielectric properties. The author made use of valuable experience gained by Yamanaka [5] in the study of other materials.

3.1. Description of apparatus

In order to obtain a possibly uniform electric field a system of flat electrodes located in a cubicoid $8 \times 4 \times 4$ cm^3 glass vessel has been used. The d.c. voltage was supplied from a stabilized supply permitting continuous control from 0–600 V at a permissible current of 500 mA.

The glass vessel filled with suitably prepared suspension was located on the heating plate of an electromagnetic mixer. The whole apparatus was inside the chamber of a special thermostat whose temperature could be controlled from 0°C to 50°C.

3.2. Choice of the dispersed phase

Electrophoretic deposits were obtained by preparing suspensions in such liquids as ethyl alcohol, methyl alcohol, propyl alcohol, amyl alcohol, acetone, distilled water, and

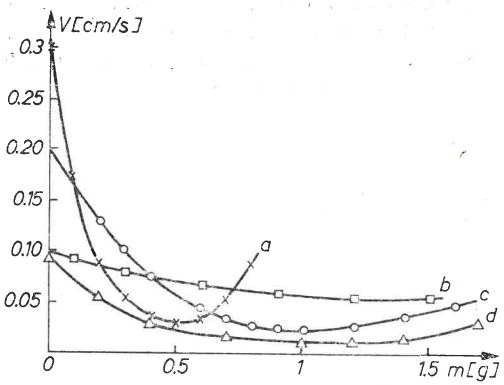

Fig. 1. Dependence of falling down velocity (v) of $BaTiO_3$ particles in alcohol on the mass (m) of 2-normal HCl added to 100 cm^3 of suspension. The concentration of the suspension is 10 g $BaTiO_3$ per 100 ccm of alcohol. Grain size 1 μm. a — ethyl alcohol, b — amyl alcohol, c — propyl alcohol, d — methyl alcohol

methyl acetate. In the majority of cases the dispersed phase fell down quite rapidly on the bottom of the vessel. A significant improvement of the stability of the suspensions has been obtained by:

a) Addition of electrolyte

Fig. 1 shows as an example the relation between the falling down velocity of $BaTiO_3$ grains and the HCl contents in the suspension. Fig. 2 illustrates the dependence of the mass of $BaTiO_3$ powder deposited on the electrode and the current density on the HCl contents in the suspension.

b) Addition of modifying agents

Addition of small amounts fo such substances as nitrocellulose, methyl polymetacrylate, or 4% collodion considerably increased the stability of the suspension. At the

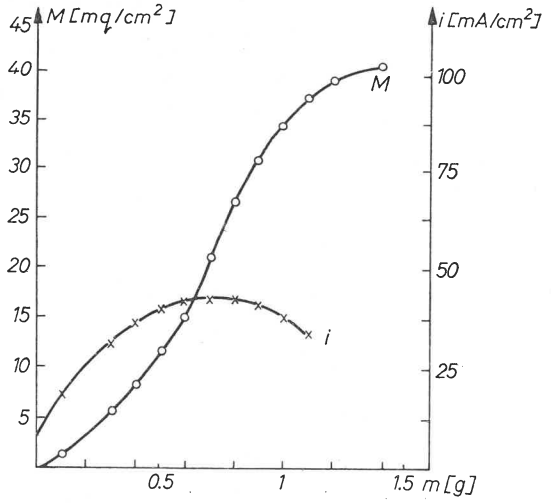

Fig. 2. Dependence of the mass (*M*) of the $BaTiO_3$ deposit on the electrode and the density of the electrophoresis current (*i*) on the amount of HCl (*m*) added to 100 g of ethylalcohol. Electrophoresis conditions: time — 30 s, field strength — 100 V/cm, concentration of suspension — 15 g $BaTiO_3$ per 100 g of alcohol, grain size 1 μm

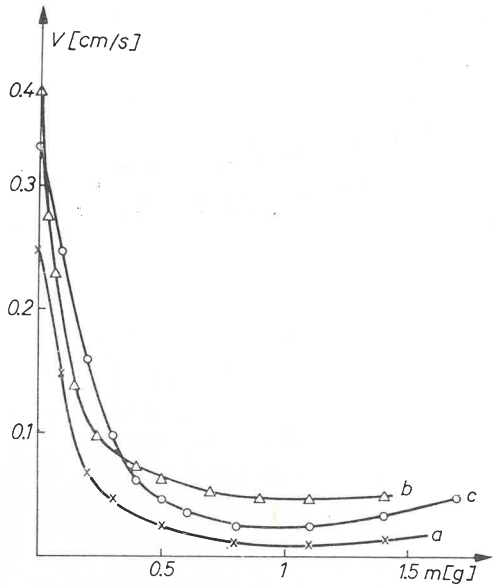

Fig. 3. Influence of methyl polymetacrylate contents (*m*) on the falling down velocity (*V*) of: *a* — $BaTiO_3$ powder, *b* — $PbZrO_3$ powder, *c* — $PbTiO_3$ powder in acetone suspension. Concentration of suspension 15 g of powder per 100 ccm of acetone

same time these agents served as bonding agents which bonded the deposited film with the metal substrate. Fig. 3 shows the dependence of the falling down velocity of the particles of the dispersed phase on the mass of the colloidal substance.

An example of the composition of a suspension from which films with sufficiently good parameters have been obtained, is given below: methyl acetate — 100 cm^3, $BaTiO_3$ powder — 20 g, nitrocellulose — 2 g, distilled water — 5 cm^3, 2n-HCl — 1 cm^3, methyl alcohol — 10 cm^3. It was possible to increase the elasticity of the deposited thin film by adding about 1 g of flaxseed oil to the suspension.

The addition of modifying agent ensures smoothness of the surface of the ferroelectric thin film and decreases its porosity and hygroscopicity.

3.3. Choice of parameters of electrophoretic deposition

It has been found in addition that the mass of the electrophoretic deposit considerably depends on the initial concentration of the suspension (C_0), deposition time (t), the applied voltage (V), distance of electrodes (d), viscosity coefficient (η), the dielectric constant of the dispersion medium (ε) and the electrokinetic potential (ξ). In some range of the values of these parameters the following relationship is satisfied:

$$m = \frac{\varepsilon V t k_0 \xi}{d\eta} \alpha$$

where m is the mass of the deposit per 1 cm^2 of the surface of the electrode and α the probability of the deposition of the particle on the electrode. The coefficient α has been defined as the ratio of the mass deposited on the electrode to that which should be deposited theoretically (*i.e.* assuming that $\alpha = 1$).

Owing to the necessity of thermal treatment of the thin film in oxygen atmosphere the most frequently used electrode was platinum in spite of the fact the attachment to the latter is the best ($\alpha = 0.9$).

It has been found that electrophoretic deposition occurs already for electric field strength of the order of 10 V/cm but if the field strength is greater than 300 V/cm a considerable fraction of the dispersed phase settles down on the bottom of the vessel near the electrode while the latter is covered by the powder in a very nonuniform way.

As it has been already mentioned before the process of electrophoretic deposition is strongly influenced by the composition of the suspension. The powder contents per 100 ccm of liquid phase should not exceed 30 g in case of $BaTiO_3$, 20 g $PbTiO_3$ and 10 g for $PbZrO_3$.

It has been shown in various experiments that the deposition conditions can be chosen so that the film thickness will be proportional to the electrophoresis time only.

In the present paper the following deposition times have been used to obtain films with thickness ranging from 1 μm to 100 μm:

for suspensions containing $BaTiO_3$ from 1 to 20 min
for suspensions containing $PbTiO_3$ from 1 to 15 min
for suspensions containing $PbZrO_3$ from 0.5 to 10 min

3.4. Electrophoretic current

Joule's heat produced during electrophoresis gives rise to changes in such parameters as the viscosity or the dielectric constant of the dispersion medium. This effect considerably hinders the possibility of obtaining films with parameters repeatable in respect of thickness and density. The temperature was thus stabilized by carrying out the experiment at a temperature lower than that of the surroundings while the current density remained small (not exceeding 10 mA/cm²). The current during the electrophoresis process does not remain constant; it tends to decrease. In identical electrophoresis conditions the

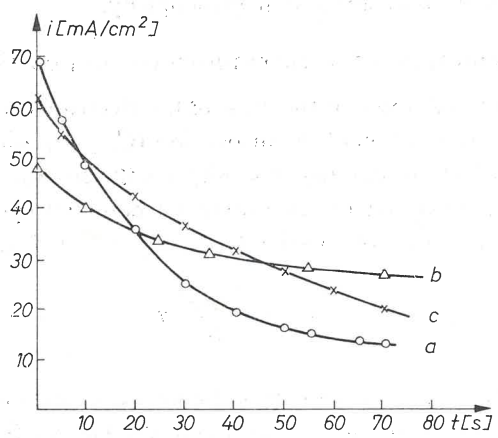

Fig. 4. Time dependence of the electrophoretic current in acetone suspension of *a* — $BaTiO_3$, *b* — $PbTiO_3$, *c* — $PbZrO_3$. Concentration of suspension: 15 g of powder per 100 ccm of acetone. Grain diameter: abt. 1 μm, field strength: 100 V/cm

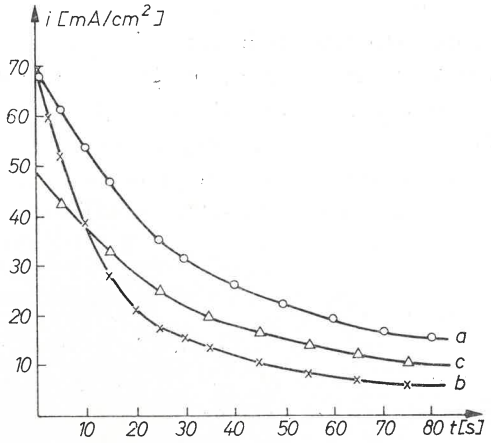

Fig. 5. Influence of mean grain size of $BaTiO_3$ powder on the time changes of the electrophoretic current density: *a* — grain diameter: from 0.5 μm to 10 μm, *b* — grain diameter: from 7 μm to 10 μm, *c* — grain diameter: from 0.5 μm to 1 μm

initial value of the current depends on the dispersion medium and is approximately proportional to the electrokinetic potential (Fig. 4).

Changes in the current during deposition also depend on the homogeneity of grains of the dispersed phase in the suspension (Fig. 5). The decrease in the current in case of powder of different grain size (from 0.5 to 10 μm) is much slower than in case when only one grain size fraction (*e.g.* 1–3 μm) is used in the preparation of the suspension. This is due to the development of the process of formation of the layer deposited on the electrode. Namely, as it has been shown by microscopic observations during the deposition of the dielectric film the latter is formed first by the deposition of micelles with greatest dimensions

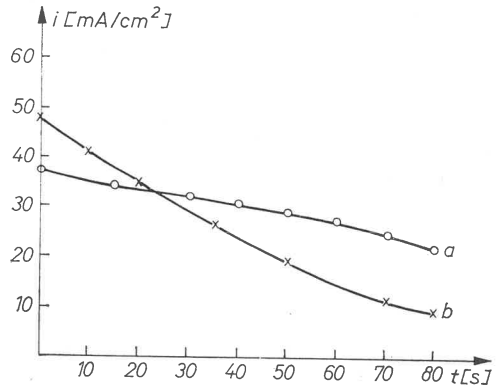

Fig. 6. Time changes of the electrophoretic current when using cathodes from: *a* — metallic copper, *b* — oxidated copper

and only after that much smaller particles enter in the pores formed in this way. This, of course, is only possible in case of powder od different grain size. The smallest particles which are electrically charged arrive at the electrode and counteract the sudden decrease in the current. They also exert considerable influence on the degree of packing and on the density of the dielectric film.

Fig. 6 shows the time dependence of the electrophoretic current in case of

a) a copper electrode,

b) copper electrode covered with oxide layers produced as a result of roasting.

The analysis of these dependences indicates that the changes in the current during the electrophoresis process are probably also influenced by the polarization of the cathode by hydrogen ions.

4. Influence of roasting temperature on the properties of thin films

In case of deposition of thin films without adding bonding agents to the suspension it was necessary to subject the films to roasting which strongly influenced their adhesion to the metallic substrate, and last not least, favourably influenced some electric properties

TABLE III

Influence of roasting temperature on the properties of thin films

Material	600°C			900°C			1350°C		
	d [g/cm^3]	ε	tg δ	d [g/cm^3]	ε	tg δ	d [g/cm^3]	ε	tg δ
$BaTiO_3$	4.2	510	0.07	0.9	720	0.02	5.4	820	0.01
$PbTiO_3$	5	45	0.09	6.2	72	0.06	7	110	0.04
$PbZrO_3$	4.7	65	0.08	6	87	0.05	7.9	120	0.03

of the film such as the breakdown voltage, permittivity and dielectric loss tangent. This is illustrated in Table III.

The roasting process was carried out in a silite furnace by keeping the film on platinum substrate for three hours at high temperature. $PbTiO_3$ and $PbZrO_3$ were roasted in lead vapour atmosphere under a nickel crucible.

5. *Final remarks*

In the present paper the author did not pay much attention to the electric properties of the ferro- and antiferroelectric thin films. Nevertheless it follows from the values of some parameters given in the Tables that the thin films obtained satisfy the conditions required in case of dielectric and insulating materials.

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