JOURNAL OF MATERIALS SCIENCE **32** (1997) 803–807

Electrolytic PZT films

I. ZHITOMIRSKY, L. GAL-OR, A. KOHN
Israel Institute of Metals, Technion-Israel Institute of Technology, Haifa, 32000, Israel
M. D. SPANG
Clausthal University, Clausthal-Zellerfeld, D3392, Germany

A novel method of cathodic deposition of complex oxide compounds has been demonstrated on the deposition of ferroelectric PZT films. In the proposed approach, PZT film formation on graphite and carbon fibre mat substrates was achieved via a peroxoprecursor. It was established that the atomic ratio of lead, zirconium and titanium in the deposit closely corresponded to that in the starting solutions. Formation of a perovskite PZT phase was observed at 500 °C. By variation of current density and deposition time the amount of the deposited material could be controlled. It was established that films obtained from solutions with hydrogen peroxide as an additive showed less tendency to crack.

1. Introduction

The formation of ceramic films by electrodeposition has received considerable attention during recent years [1–10]. This method of ceramic processing is especially attractive for the formation of thin ferroelectric films [8–12] owing to low capital investment costs, as well as rigid control of film thickness, uniformity and deposition rate [1, 8]. Electrodeposition can be performed by both cathodic [11, 12] and anodic methods [8]. A great deal of recent research has focused on anodic electrodeposition, including the hydrothermal–electrodeposition method [9, 10]. However, this approach is limited by the necessity to use titanium [8, 9] substrates or layers [10]. Cathodic electrodeposition holds great promise for electronic device development due to the possibility of film formation on various substrates. The feasibility of cathodic electrodeposition of important ferroelectric materials such as $BaTiO_3$ [11] and PZT [12] has been demonstrated. Despite the obvious advantages of this method, difficulties related to the control of deposit stoichiometry arise as a result of the different deposition rates of the individual components.

In the cathodic electrodeposition process, metal ions are hydrolysed by an electrogenerated base to form oxide/hydroxide films on the cathodic substrate. Different cathodic reactions can be utilized for base generation [1, 4, 5, 7, 11, 12]. It should be noted that water and nitrates are important cathodic reactants. A significant problem is associated with the use of titanium salts which immediately react with water to form a titanium hydroxide precipitate. Moreover, titanium nitrate is not a stable compound. In the light of the above, the major problem with titania electrodeposition is related to the use of water and nitrates as sources of OH^- groups in the cathodic process.

In a previous work [13] it was established that electrodeposition of titanium oxide films can be performed via a peroxoprecursor. The peroxocomplex of titanium is stable under certain conditions in aqueous solutions [14] and can be hydrolysed by an electrogenerated base [13] to form a hydroxoperoxocompound deposit, thermal decomposition of which, in turn, results in the formation of titania films. In this way, the problem of titania cathodic deposition was solved by use of a titanium peroxocomplex instead of titanium ion. As an extension of this work, experiments were performed on electrodeposition of zirconium titanium double oxide [15]. It was revealed that the use of the peroxoprecursor approach provides the same deposition rate of individual components and $ZrTiO_4$ films of exact stoichiometry were obtained after thermal treatment of the deposit at low temperature, in accordance with the temperature of formation of this material via the wet chemical method. Experimental results obtained on the electrodeposition of $ZrTiO_4$ pave the way for the deposition of PZT films. With this in mind, the present investigation was carried out to study cathodic electrodeposition of PZT via a novel peroxoprecursor route.

2. Experimental procedure

As starting materials, commercially guaranteed salts of $TiCl_4$, $ZrOCl_2 \cdot nH_2O$, $Pb(NO_3)_2$ and hydrogen peroxide H_2O_2 (30 wt % in water) were used. Water solutions of these materials (stock solutions) mixed in a ratio $Pb(NO_3)_2:ZrOCl_2:TiCl_4:H_2O_2 = 1:0.52:0.48:2.4$ were prepared; $Pb(NO_3)_2$ concentration was 0.005 M. Experiments were also performed with 0.05–0.5 M additives of H_2O_2 to the stock solutions in order to study the possible effect on deposit morphology. Graphite plates (20 × 10 × 2 mm) and carbon fibre mats (40 × 10 × 0.5 mm) supplied by Lydall Inc. were used as substrates. The graphite specimens were polished with a 1000 grit SiC abrasive paper, rinsed with ethanol in an ultrasonic bath, then washed with distilled water and dried in air. Carbon fibre mat

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specimens were used as-received. The electrochemical cell included the cathodic substrate centred between two parallel platinum counter electrodes. Electrodeposition experiments were performed at 2 °C. Cathodic deposits were obtained at constant current densities ranging from 5–60 mA cm^{-2}. Deposition times were in the range of up to 5 min. The cell voltage was recorded during the deposition process. After drying at room temperature the as-deposited films were annealed in air for 1 h at various temperatures. Cathodic polarization curves were obtained with a potentiostat (Princeton Applied Research, model 350A) at 2 mV s^{-1} scan rate. The microstructure and composition of obtained films were studied using a scanning electron microscope (Jeol, model JSM-840) equipped with EDS. The phase content was determined by X-ray diffraction with a diffractometer (Phillips, model PW-1820) using monochromatized CuK_α radiation at a scanning speed of 0.4° min^{-1}.

3. Results

The experiments revealed film formation on the graphite substrate. Fig. 1 shows cell voltage–time curves obtained at different current densities. During the deposition process the cell voltage was found to increase with time. Such a voltage behaviour is attributed to the increase in deposit resistivity with time owing to increase of the deposit thickness. Moreover, a continuous voltage increase usually indicates the absence of a deposit spallation process [3], which brings about anomalies in voltage behaviour. As could be expected, deposition at higher current densities requires higher voltages. Fig. 2 shows deposit weight versus current density at constant deposition time. A nearly linear dependence was obseved, as could be expected on the basis of Faraday's law. The deposit weight was also traced as a function of deposition time. The results given in Fig. 3 indicate that, for time periods ranging up to 3 min, deposit weight increases linearly with time at constant current density. At higher deposition times, the deposite rate becomes slower. Fig. 4 shows a cathodic polarization curve for graphite versus a saturated calomel electrode (SCE). Two polarization regions can be distinguished on this curve, which were attributed to different cathodic reactions. Fig. 5 shows X-ray diffraction patterns of "green" deposits and deposits subjected to thermal treatment at different temperatures. As-prepared films were found to be amorphous as indicated by the absence of any well-defined diffraction peaks in the XRD patterns apart from peaks of the substrate. The study of phase evolution of obtained films revealed the formation of a perovskite phase at 500 °C. It should be pointed out that the thermal treatment at 500 °C and at higher temperatures resulted in burning out of the substrate and XRD studies were performed on powder specimens. It is important to note that at 500 °C and higher, XRD patterns show only peaks of a perovskite PZT phase. No evidence of peaks of individual oxides or pyrochlore phase was observed in our experiments. EDS analyses have been performed on powders obtained after thermal treatment of specimens at 800 °C for 1 h. Numerous experiments have shown that the composition of these powders is PbO 50.0–51.0, ZrO_2 25.0–26.5, TiO_2 22.9–24.4 mol %.

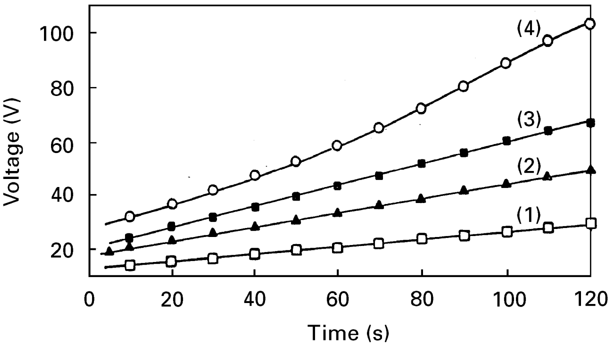

Figure 1 Cell voltage as a function of deposition time at different current densities: (1) 20, (2) 30, (3) 40, (4) 60 mA cm^{-2}.

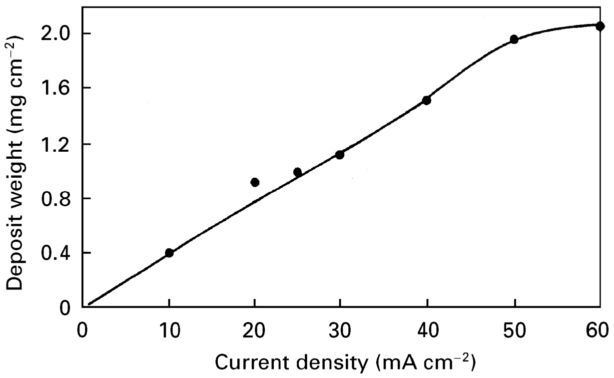

Figure 2 Deposit weight as a function of current density at constant deposition time of 2 min.

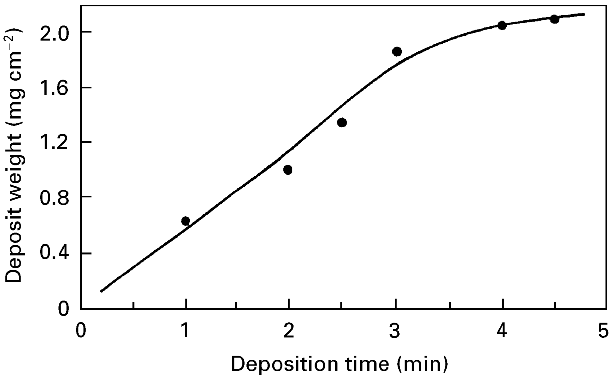

Figure 3 Deposit weight as a function of deposition time at constant current density of 25 mA cm^{-2}.

Obtained films were submitted to SEM examination. According to SEM observations, deposits of different thicknesses up to 10 μm were obtained on the graphite substrates. Fig. 6a shows a scanning electron micrograph of the "green" deposit on a graphite substrate. The ultrafine size of the deposit particles is noteworthy, and far below the micrometer scale. However, microscopical observations indicated development of cracks, which appear due to drying shrinkages. X-ray dot maps for individual elements indicate

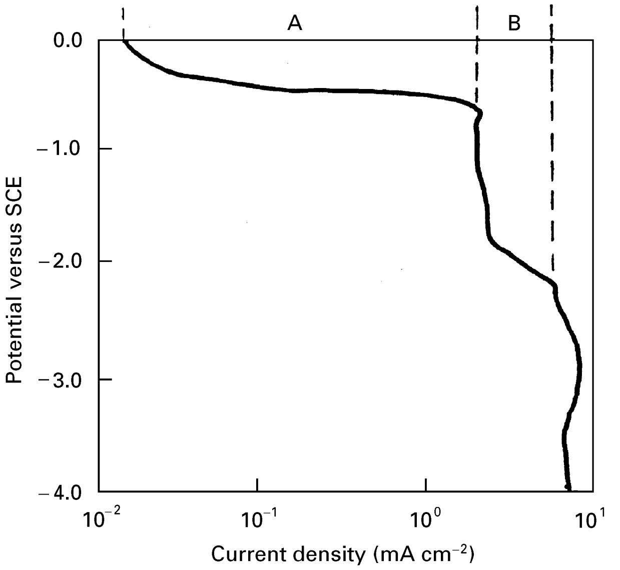

Figure 4 Cathodic polarization curve for graphite at 2 mV s^{-1} scan.

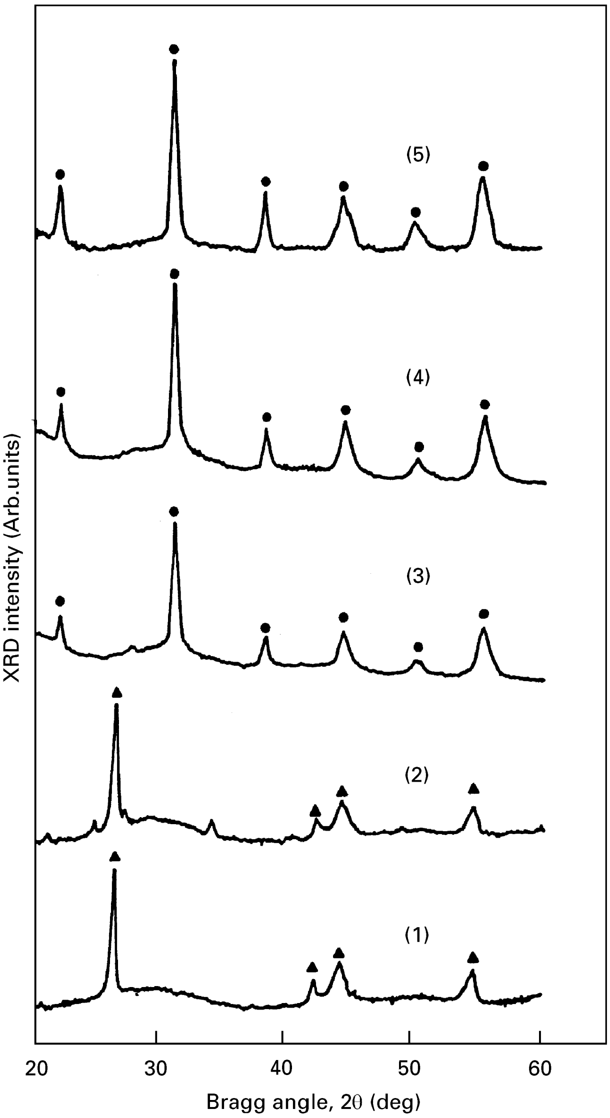

Figure 5 X-ray diffraction patterns of deposits obtained at current density of 25 mA cm^{-2}: (1) "green" deposit, and after thermal treatment at different temperatures for 1 h: (2) 250, (3) 500, (4) 600, (5) 800 °C (at 500 °C the substrate is burnt out). (▲) Substrate, (●) PZT.

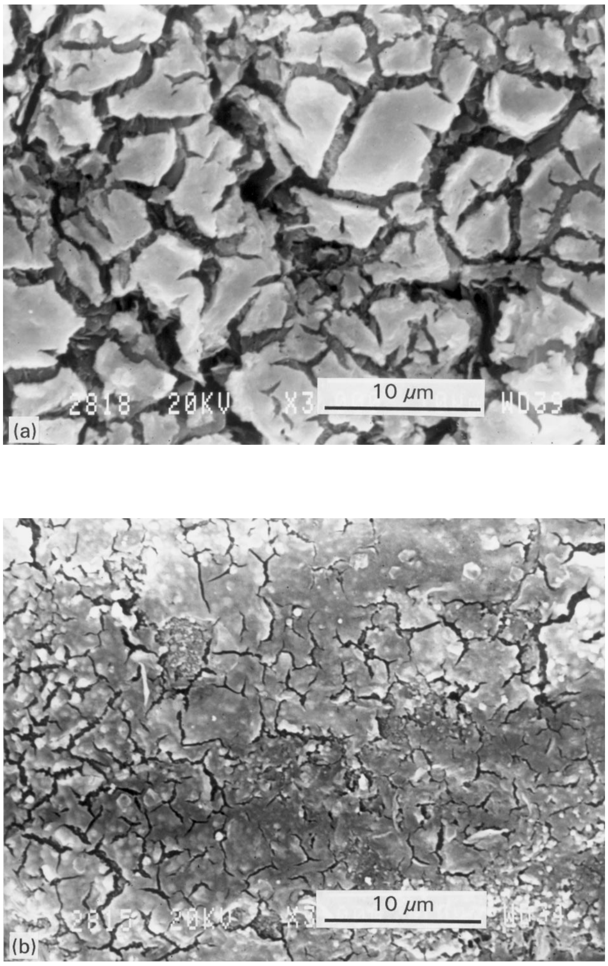

Figure 6 Scanning electron micrographs of "green" deposit on the graphite substrate, obtained from stock solution (a) without additive and (b) with 0.05 M hydrogen peroxide additive.

that lead, titanium and zirconium are homogeneously distributed throughout the film. It was established that the addition of hydrogen peroxide results in improvement of the film morphology. Fig. 6b shows a scanning electron micrograph of the deposit obtained from the solution containing 0.05 M hydrogen peroxide. Note that specimens shown in Fig. 6a and b have nearly the same deposit weight and, as could be expected, the same thickness. It should be pointed out that the microstructure evolved in electrodeposition experiments performed with the additive is more continuous and uniform with significantly less cracking. With experimental techniques used we have found no difference in composition and phase evolution of specimens prepared with or without this additive. Further increase in the amount of hydrogen peroxide has not resulted in an appreciable improvement of deposit morphology. It should be noted that film morphology was strongly influenced by the relative roughness of the surface of the substrate used. Indeed, it was observed that pores and other defects in the substrate, initiated cracking.

Electrodeposition experiments revealed the feasibility of film formation on carbon fibre mats. An effective area of fibre mat specimens was used for calculation of the current density. Fig. 7 shows scanning electron micrographs of the deposits obtained on the carbon fibre mat specimens. At current density of

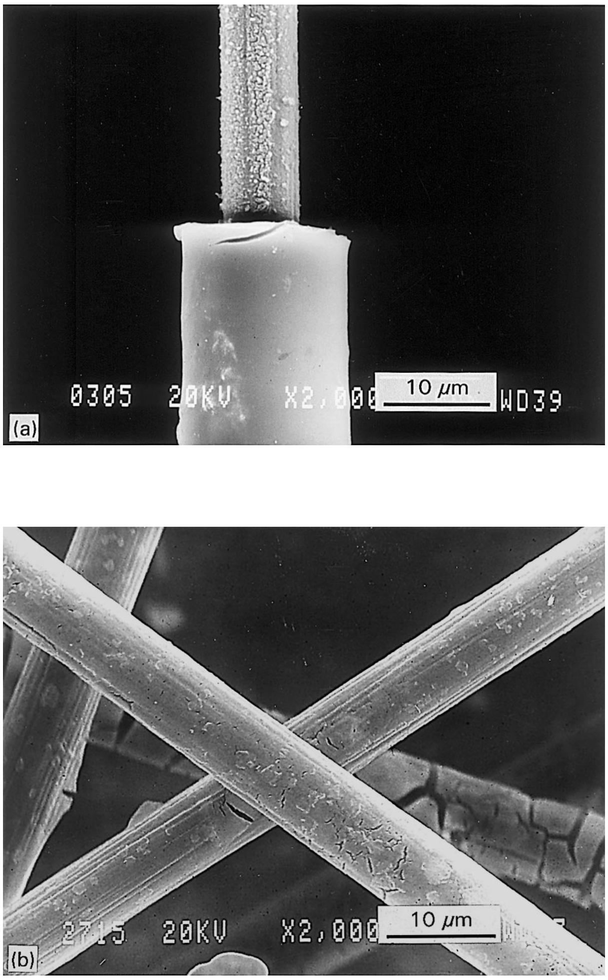

Figure 7(a, b) Scanning electron micrographs of "green" deposit on a carbon fibre mat.

25 mA cm^{-2} and deposition time of 1 min, a film thickness of about 1 μm could be achieved. One of the important observations is that all fibres were uniformly coated. By variation of deposition time, deposits of different thickness up to 5 μm were obtained. However, at a deposit thickness higher than 1–2 μm, crack formation was observed during the drying stage. It was also seen that deposits obtained from solutions containing additional amounts of hydrogen peroxide exhibit less tendency towards cracking.

4. Discussion

An important point to be discussed is the electrochemical mechanism of film formation. The two different regions in the polarization curve can be attributed to cathodic reactions discussed in the literature [1, 4, 5, 7, 11, 12]. The first region (A) is most likely attributed to reduction reactions consuming H$^+$ [1, 11, 12]. These reactions, as pointed out elsewhere [12], cause only a slight increase of pH at the cathode region. At higher absolute values of the potential (region B) the following cathodic reactions can be considered

$$NO_3^- + H_2O + 2e^- \rightleftharpoons NO_2^- + 2OH^- \quad (1)$$

$$NO_3^- + 6H_2O + 8e^- \rightleftharpoons NH_3 + 9OH^- \quad (2)$$

$$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^- \quad (3)$$

$$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^- \quad (4)$$

These reactions consume H_2O and generate OH^-. Reactions 1–4 result in a significant increase of pH value near the cathode and are important for the deposition process. In contrast to other work [12], no region in the polarization curve related to lead metal deposition was observed in our experiments. This is not surprising, because in recent electrodeposition experiments [16] performed with $Pb(NO_3)_2$ solutions, it was established that solution composition exerts a significant effect on the deposit content. Only by variation of electrolyte concentration and starting pH could lead metal, $Pb(OH)_2$ or PbO films be obtained. It should be pointed out that in contrast to the earlier work [16], no PbO_2 deposition on the anode was observed here. This is important in order to obtain the cathodic deposit of desired stoichiometry. The anodic reaction is supposed to be

$$2H_2O \rightleftharpoons O_2 + 4H^+ + 4e^- \quad (5)$$

It should be mentioned that in experiments on electrolytic film deposition from $Pb(NO_3)_2$ solutions [16] it was established that "green" deposits have well-defined crystalline structure of lead, $Pb(OH)_2$ or PbO, depending on the experimental conditions used. In experiments on electrodeposition of zirconia and titania [13, 15] the crystallization of films was observed at 400 °C. The co-deposition experiments performed in this work have shown an amorphous nature of the "green" deposit and the absence of peaks of individual oxides on the X-ray diffraction patterns of films subjected to the thermal treatment. It should be pointed out that phase separation is detrimental, as it allowed the formation of the stoichiometric compound only at relatively high temperatures. In contrast, in this work as well as in previous experiments on electrodeposition of $ZrTiO_4$ films [15] no phase separation was observed. Thermal treatment of "green" deposits resulted in the formation of single-phase compounds at relatively low temperatures, in accordance with the temperatures of the formation of corresponding compounds via the wet chemical method of powder processing. On the basis of EDS studies, it can be concluded that the atomic ratio of lead, titanium and zirconium in the deposits nearly corresponds to that in the starting solutions.

Turning again to the experiments on powder formation via wet chemical methods [17, 18] it should be mentioned that the use of peroxoprecursor was found to improve co-precipitation [18] and allows different complex oxide compounds of desired stoichiometry to be obtained [17–22]. The analogy of film formation via the peroxoprecursor route in this work, as well as in previous studies, and formation of powders of corresponding materials in wet chemical methods [17, 18] is especially evident, taking into account that the difference between these processes consists only in the origin of the base, which in electrodeposition experiments is generated at the cathode. The mechanism of deposition can be envisioned as hydrolysis of solutions by the electrogenerated base, formation of colloidal particles of peroxoprecursor near the cathode, and their subsequent electrophoretic motion toward the cathode, resulting in the formation of the deposit. On the basis of XRD, EDS and X-ray dot mapping experiments performed in this work, and previous results of electrodeposition via peroxoprecursors [13, 15], it can be supposed that obtained "green" deposits have a complex nature [17, 18]. As a result of the thermal decomposition of the complex precursor, formation of PZT films was observed at 500 °C. Such a low formation temperature is important for integration of films in different electronic devices.

The focus of the present study was to examine the novel approach to the electrodeposition of PZT films and no special precautions were taken in this work to prevent cracking. However, an important finding was that the hydrogen peroxide additive influenced the film morphology. One possible reason might be that the additive allows improvement of the deposit adhesion. In our preliminary experiments on electrodeposition of $BaTiO_3$ films, a similar effect has been observed. In relation to experiments on the ceramic coating development by the soaking technology [23], it should also be mentioned that pretreatment of carbon fibres in hydrogen peroxide before coating has been used for carbon activation and was found to increase the deposit yield. According to the review [24] of thick sol–gel coatings, film adhesion is of significant importance for preparation of thick, crack-free deposits. Therefore, it is reasonable to expect that the presence of additional amounts of hydrogen peroxide in the solutions provides better deposit adhesion which, in turn, influences the deposit morphology. Further experiments are necessary for optimization of the drying process in order to prevent cracking.

Although the feasibility of the deposition of oxide films via the peroxoprecursor route has been proved by this work and by previous studies [13, 15], additional work is necessary for fundamental understanding regarding the exact mechanism of deposition and the structure of the complex deposit. In this work we have used graphite and carbon fibre mat substrates for the development of the deposition process. Obtained results have practical importance for the development of composite materials. Indeed, the use of burnable fibrous templates allows desired phase connectivity to be achieved and advanced piezoelectric composites to be obtained [25]. In this respect, the deposition method developed in this work could become important for impregnation of fibrous materials and the formation of uniform coatings of controlled thickness on fibrous structures. For important applications in different electronic devices the electrodeposition process should be applied to platinized silicon substrates. So far, cathodic electrodeposition of PZT and $BaTiO_3$ has been performed on stainless steel, iron, nickel and titanium electrodes [11, 12]. Difficulties were pointed out with deposition on platinum substrates. It was clarified that the use of the peroxoprecursor approach allows problems related to deposition of these materials on platinum to be avoided. Results of experiments performed on electrodeposition of these materials on platinum substrates will be submitted for publication in the near future.

5. Conclusion

Results obtained have shown that the method of electrodeposition of ceramic oxide films via a peroxoprecursor developed in previous works can be extended to the deposition of PZT films. PZT film deposition has been demonstrated on graphite and carbon fibre mat substrates. It was established that the atomic ratio of individual components in the deposit nearly corresponds to that in the starting solutions. The proposed method has promising possibilities owing to the low temperature of PZT film crystallization (500 °C), the possibility of the control of stoichiometry and the amount of the deposited material. In addition, uniform film formation can be achieved on substrates of complicated shapes.

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Received 22 December 1994
and accepted 13 February 1996