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Electrolytic Deposition of Oxide Films in the Presence of Hydrogen Peroxide

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Abstract

Cathodic electrosynthesis of TiO_2, Nb_2O_5, PZT, composite RuO_2–TiO_2 and Al_2O_3–TiO_2 films and powders was performed. In the proposed approach, TiO_2, Nb_2O_5, PZT film formation on platinized silicon or/and Pt substrates was achieved via peroxo-precursors. Obtained deposits were characterized by XRD, SEM, Auger and SIMS methods. The crystallization behaviour of the deposits has been studied. Possible cathodic reactions which underlie the deposition process and the role of hydrogen peroxide are discussed. © *1999 Published by Elsevier Science Limited. All rights reserved*

Keywords: Nb_2O_2, PZT, TiO_2, ZrO_2, RuO_2, electrolytic deposition.

1 Introduction

During recent years, interest has been generated in electrolytic deposition of ceramic films.[1–14] This technique can be considered as an important tool in the formation of nanostructured materials, including monolayer and multilayer films, powders and composites.[6,7,10,11,13] Cathodic electrodeposition offers important advantages[2,15] and holds great promise for various applications. A great deal of recent research has been devoted to demonstrating the feasibility of electrodeposition of important ceramic materials.[1–20] Cathodic electrodeposition is achieved via hydrolysis of metal ions or complexes by electrogenerated base to form oxide,[1,6,12,15] hydroxide[3,10,11,16,17] or peroxide[2,7,9,13,18–20] deposits on cathodic substrates. Hydroxide and peroxide deposits can be converted to corresponding oxides by thermal treatment. Formation of oxide materials via corresponding hydroxides or peroxides constitute two different chemical routes in electrodeposition. In previous work[16] electrodeposition of zirconia was performed via hydroxide and peroxide precursors and obtained results were compared. It should be noted that peroxoprecursor method cannot be applied for deposition of such materials as RuO_2,[17,21] as Ru species bring about decomposition of H_2O_2 in solutions. On the other hand peroxoprecursor route was designed in order to solve problems associated with the electrodeposition of TiO_2[2,7,13,21] and Nb_2O_5.[18] These materials can be deposited via corresponding peroxides. The important finding was that complex oxide compounds such as $ZrTiO_4$ and PZT can be deposited via peroxoprecursors.[9,13,19,20] It was revealed that the use of the peroxoprecursor approach allows to obtain deposits of desired stoichiometry. $ZrTiO_4$ and PZT films were obtained after thermal treatment of obtained precursors at relatively low temperatures, in accordance with the temperatures of formation of these materials via the wet chemical method. However, further investigations are necessary to obtain a better understanding of the mechanism of deposition via peroxoprecursors.

This paper presents results of electrodeposition of ceramic materials in the presence of hydrogen peroxide and addresses different factors controlling deposit composition, morphology and crystallization behaviour.

2 Experimental Procedures

As starting materials commercially guaranteed $TiCl_4$ (Merck), $NbCl_5$ (Fluka Chemie AG), $ZrOCl_2{\cdot}8H_2O$ (Fluka Chemie AG), $RuCl_3{\cdot}nH_2O$ (Fluka Chemie AG), $AlCl_3{\cdot}6H_2O$ (Aldrich Chemical Company, Inc), $Pb(NO_3)_2$ (Riedel -de Haen) and hydrogen peroxide H_2O_2 (30 wt% in water,

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Carlo Erba) were used. 0·3 M $TiCl_4$ solution in methyl alcohol was prepared at 1°C, then H_2O_2 was slowly added (H_2O_2:$TiCl_4$ = 20:1). At this stage significant gas evolution was observed, attributed probably to the following reaction:[22]

$$3H_2O_2 + 2HCl \Rightarrow 4H_2O + O_2 + Cl_2 \qquad (1)$$

After aging at 20°C for 3 days this solution was diluted with water and methyl alcohol to obtain stock solution 1 (Table 1). Procedures for preparation of stock solutions 2–9 (Table 1) were similar to those described in previous papers.[18,20,21,23] Electrodeposition was performed at a galvanostatic regime. The electrochemical cell for deposition included the cathodic substrate centered between two parallel platinum counterelectrodes. Pt foils, platinized silicon wafers (Pt/Ti/SiO_2/Si, 1600 Å Pt, 400 Å Ti, 1000 Å SiO_2), Ti and graphite plates were used as cathodic substrates. Obtained deposits were washed with water in order to prevent Cl impurity in the solution. Multilayer deposition was performed in order to decrease cracking attributed to drying shrinkage. The microstructure of the obtained deposits was studied using a scanning electron microscope (Jeol, JSM-840) equipped with EDS. X-ray diffraction patterns were obtained using a diffractometer (Phillips, PW- 1820, CuK_α radiation). For the X-ray studies the deposits were annealed in air at various temperatures. Thin films were also studied by Auger method (scanning microscope Perkin–Elmer, PHI model 590A) and SIMS method (Cameca IMS 4F ion microscope).

3 Results and Discussion

In the cathodic electrodeposition method,[1–3] the following reactions are used to generate base at an electrode surface:

$$2H_2O + 2e^- \Longleftrightarrow H_2 + 2OH^- \qquad (2)$$

$$NO_3^- + H_2O + 2e^- \Longleftrightarrow NO_2^- + 2OH^- \qquad (3)$$

$$O_2 + 2H_2O + 4e^- \Longleftrightarrow 4OH^- \qquad (4)$$

Electrodeposition of TiO_2 and Nb_2O_5 films is achieved via hydrolysis of corresponding peroxocomplexes by electrogenerated base and thermal decomposition of obtained peroxoprecursors.[2,7,13,18] In contrast to Refs. 2,7 and 13 in this work electrodeposition of titania films was performed at 20°C. Titania films were prepared from stock solution 1 on Pt foils and platinized silicon wafers. Thick deposits (up to 1–2 μm) were obtained by multiple deposition accompanied by drying at 150°C. As-prepared deposits were found to be amorphous, evidence of crystallinity was observed at temperatures exceeding 400°C. As can be seen in Fig. 1, peaks of an anatase structure[24] were observed at 500°C. SIMS analysis revealed residual Cl^- in obtained films. SIMS depth profiles of Cl^- indicated that the films contained

Table 1. Compositions of solutions and experimental conditions of the deposition process

Stock solution	*Electrolyte*	*Solvent*	*Temperature (°C)*	*Current density (mA cm^{-2})*
1	0·005 M $TiCl_4$ + 0·1 M H_2O_2	Methyl alcohol–water (3:1[a])	20	20
2	0·005 M $NbCl_5$ + 0·05 M H_2O_2	Water	1	20
3	$Pb(NO_3)_2$:$ZrOCl_2$:$TiCl_4$:H_2O_2 = 1:0·52:0·48:10 $Pb(NO_3)_2$ concentration 0·005 M	Water	1	25
4	$TiCl_4$:H_2O_2:$RuCl_3$ = 1:2:1, total concentration of Ti and Ru salts 0·005 M	Methyl alcohol–water (1:1[a])	1	20
5	$TiCl_4$:H_2O_2:$RuCl_3$ = 3:6:1, total concentration of Ti and Ru salts 0·005 M	Methyl alcohol–water (3:1[a])	1	20
6	$TiCl_4$:H_2O_2:$RuCl_3$ = 9:18:1 total concentration of Ti and Ru salts 0·005 M	Methyl alcohol–water (9:1[a])	1	20
7	$TiCl_4$:H_2O_2:$AlCl_3$ = 1:2·5:2, total concentration of Ti and Al salts 0·005 M	Methyl alcohol–water (3:1[a])	20	20
8	$TiCl_4$:H_2O_2:$AlCl_3$ = 1:2·5:1, total concentration of Ti and Al salts 0·005 M	Methyl alcohol–water (3:1[a])	20	20
9	$TiCl_4$:H_2O_2:$AlCl_3$ = 2:5:1, total concentration of Ti and Al salts 0·005 M	Methyl alcohol–water (3:1[a])	20	20

[a] Volume ratio.

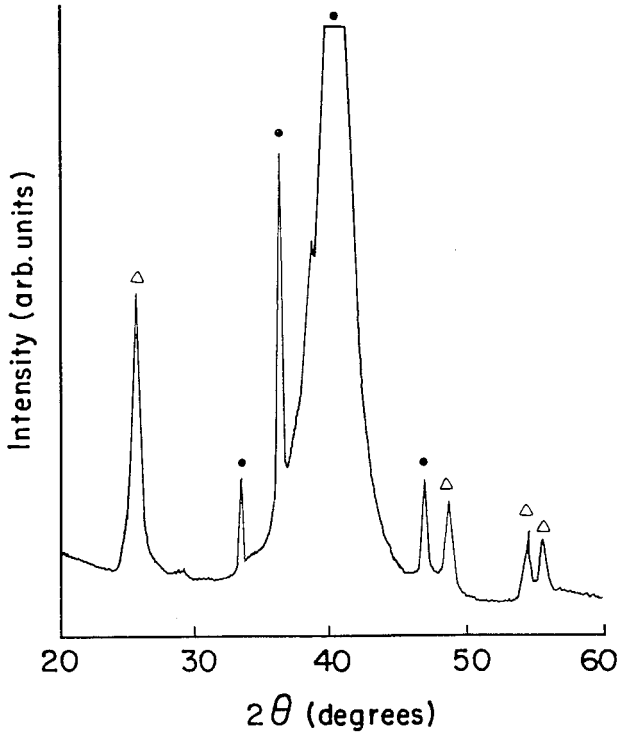

Fig. 1. X-ray diffraction pattern of titania deposit on platinized silicon after thermal treatment at 500°C for 30 min. Δ, TiO_2 (anatase); ●, substrate.

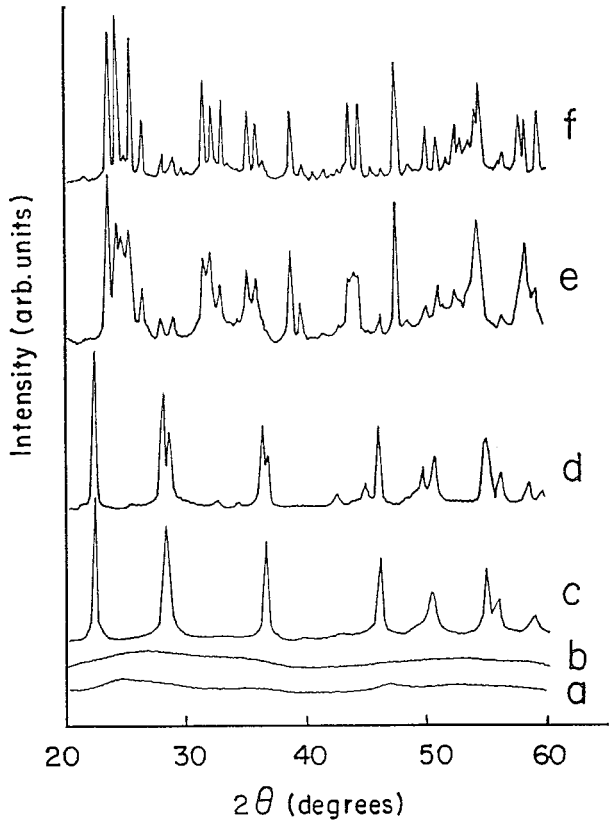

Fig. 2. X-ray diffraction patterns of niobium oxide powders: (a) as prepared, and after thermal treatment at different temperatures for 1 h: (b) 500°C, (c) 600°C, (d) 850°C, (e) 1050°C, (f) 1200°C.

0·06–0·09 at% of Cl^-. At this point it is important to mention that chloride ions can be partially removed from starting solutions through an oxidoreduction[22] process [reaction (1)]. The residual Cl^- concentration in the films was comparable with that in chemically precipitated powders obtained in the presence of H_2O_2.[25,26]

Niobium oxide deposits were obtained from stock solution 2. Thick deposits were removed from the Pt substrates for preparation of powder samples. Figure 2 shows X-ray data of the powder samples. The X-ray diffractogram of fresh deposits exhibit their amorphous nature. Crystallization of a pseudohexagonal Nb_2O_5 phase[27] was observed at 600°C. The results are in agreement with those obtained in previous work.[18] Crystallization of a pseudohexagonal Nb_2O_5 phase was also observed in Nb_2O_5 films and powders prepared by other methods.[28–30] On exposure of obtained deposits to the temperature of 850°C, X-ray diffraction patterns exhibit peaks of orthorhombic form of Nb_2O_5.[31] The formation of orthorhombic Nb_2O_5 has been observed in powders obtained by hydrothermal H_2O_2 oxidation of Nb[29] and in alkoxide-derived niobium pentoxide gels.[32] After thermal treatment at 1050°C the samples consisted of mixtures of M and H forms of Nb_2O_5.[30,33,34] According to Refs 30 and 33 M-Nb_2O_5 is considered to be a two-dimensionally ordered H-Nb_2O_5. XRD spectra taken from deposits thermally treated at 1200°C show peaks of monoclinic H-Nb_2O_5,[35] which is the only form stable at room temperature and atmospheric pressure.

Thin Nb_2O_5 films (up to 1000 Å) were smooth and adhered well to platinized silicon substrates. Typical Auger depth profile for thin Nb_2O_5 film on platinized silicon is shown in Fig. 3. As seen in Fig. 3 at ~500 Å, the oxygen peak O and niobium peak Nb begin to decrease; correspondingly the Pt peak begins to increase, signifying the beginning of the

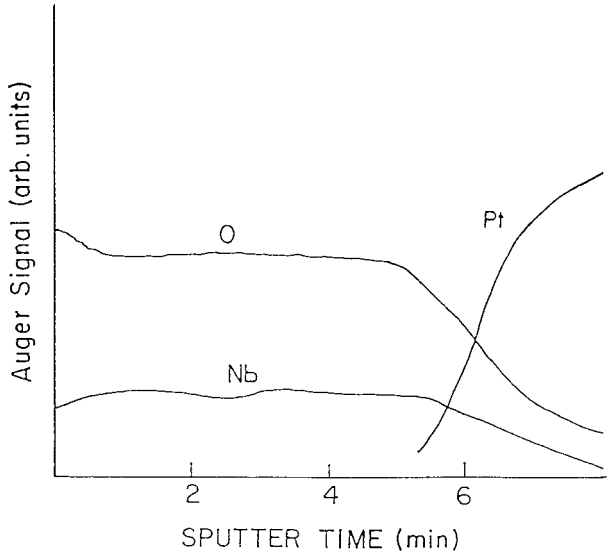

Fig. 3. Auger depth profile of green niobium oxide film on platinized silicon.

transition to platinum. The niobium oxide/platinum surface is not abrupt, but forms a region with a gradient composition. Thick films (1–2 μm) exhibited microporosity, resulting probably from the gas evolution during electrodeposition (Fig. 4).

Results of this work, coupled with previous results,[2,7,13,18] pave the way for formation of TiO_2 and Nb_2O_5 powders via electrosynthesis and electrodeposition of thin films on various substrates. The possibility of thin film formation on platinized silicon is important for electronic applications. However, further experiments are necessary for optimization of the deposition process in order to prevent microporosity and cracking. Studies in this direction are under way. The peroxoprecursor method developed first for deposition of titania and applied then for deposition of niobium oxide can be used for electrosynthesis of other oxides. Obtained results have practical importance for the development of complex compounds and composite materials. It should be noted that hydrogen peroxide suppresses hydrolysis of titanium and niobium ions,[22,36] which are however able to coprecipitate with other ions.[37–39] Turning to the experiments on powder formation via wet chemical methods it should be mentioned that the use of peroxoprecursors was found to improve coprecipitation and allows different complex oxide compounds of desired stoichiometry to be obtained.[37,40-42] The hydrogen peroxide additive has a number of effects on precipitates, such as conversion of the hydroxide precipitates into hydrated oxides or peroxides, reduction of bridging and non-bridging hydroxogroups in coprecipitates resulting in lower aggregation of dried powders[37,38] and enhancement of crystallization of complex oxides at lower temperatures.[42] According to Ref.25, addition of the H_2O_2 inhibits formation of carbonate species when precipitation is performed under a CO_2 containing atmosphere. Several previous investigations have been undertaken on the electrosynthesis complex oxide compounds via the peroxoprecursor route including comparison of crystallization behaviour of the complex oxides with the crystallization of individual components. The important finding was that complex oxide compounds such as $ZrTiO_4$ and PZT[9,13,19,20] can be deposited via corresponding peroxoprecursors. The experimental results obtained by electrogenerated base method[9,13,19,20] were similar to those obtained by wet chemical methods.[37,38,41,42] As an extension of previous works[9,20] in this work the electrodeposition of PZT was performed on platinized silicon substrates.

Obtained results of X-ray study (Fig. 5) are in a good agreement with previous works.[9,20] 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. Results of X-ray study show that PZT crystallizes directly from the amorphous phase. Typical Auger spectrum of the surface of as-prepared film is shown in Fig. 6. The spectrum revealed Pb, Zr, Ti, O and carbon as a surface contaminant [Fig. 6(a)]. After ~8000 Å sputtering

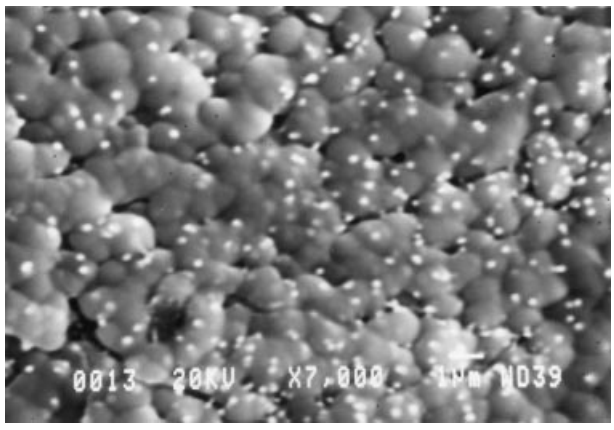

Fig. 4. SEM picture of green niobium oxide film on platinized silicon.

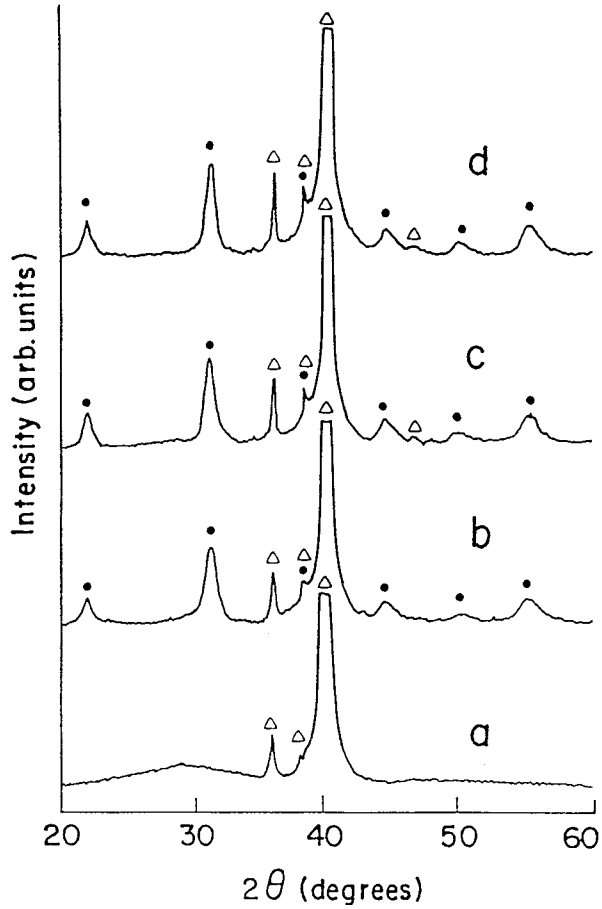

Fig. 5. X-ray diffraction patterns of PZT deposits on platinized silicon substrates: (a) as prepared, and after thermal treatment at different temperatures for 30 min: (b) 500°C, (c) 600°C; (d) 700°C. ●, PZT; Δ, substrate.

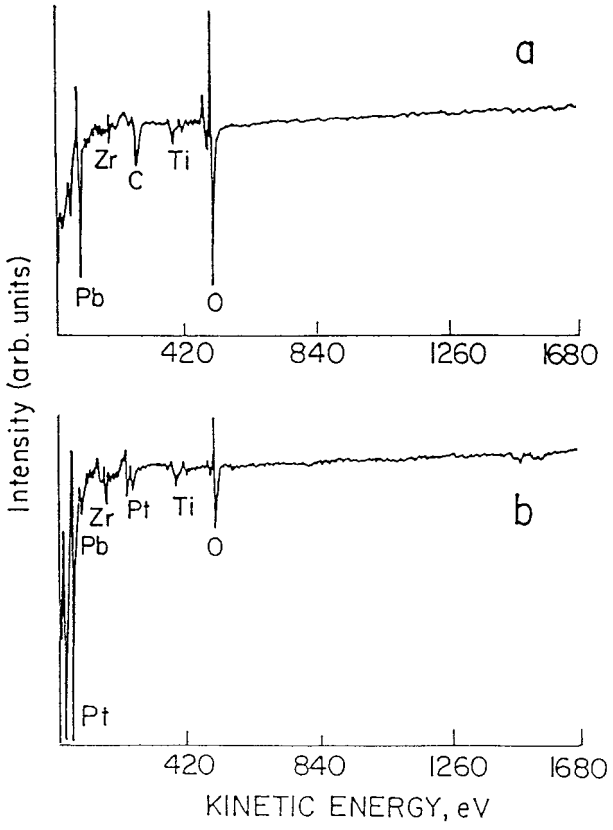

Fig. 6. Auger spectra of (a) the surface and (b) after ~ 8000 Å sputtering of PZT film on platinized silicon.

peaks of Pt were observed in addition to those of Pb, Zr, Ti and O [Fig. 6(b)]. Typical Auger depth profile for PZT film is shown in Fig. 7. Relatively uniform distribution of Ti, Zr and Pb was observed. It should be noted that for important applications of ferroelectric films in different electronic devices the electrodeposition process should be applied to platinized silicon substrates. However, no cathodic deposition of complex titanates on Pt was achieved in other works.[43,44] It is expected that other complex titanates and niobates can be deposited via the peroxoprecursor route.

The feasibility of the deposition of titania films is important for electrodeposition of composite materials. Composite RuO_2–TiO_2 and Al_2O_3–TiO_2 materials were obtained from stock solutions 4–9. Figure 8 shows EDS spectra for deposits obtained from stock solutions 4–9 (deposits 4–9). Ru/Ti ratio was found to be 0·9, 0·6 and 0·1 for deposits 4, 5 and 6, respectively, obtained on Pt and TI substrates. The feasibility of cathodic electrodeposition of composite RuO_2–TiO_2 films on Ti substrates is important for electrochemical applications.[45–47] Al/Ti ratio was found to be 2·9, 1·3 and 0·6, for deposits 7, 8 and 9, respectively, on graphite substrates. Figure 9 shows SEM pictures of deposits 5 and 6 which were removed from Pt substrates and thermally treated at 600°C for 1 h. Obtained powder samples contained platelets of uniform thickness in the range of up to 5 μm.

Cathodic electrodeposition process is based on base generation in electrode reactions and neutralization of ionic species to form deposits. During the deposition process an insulating layer forms, which prevents OH^- generation. Coating resistivity is a major limiting factor of the electrodeposition method for development of thick coatings. According to Ref.1 insulating ceramics form very thin films or porous films. However, it is known that RuO_2 exhibits metallic resistivity.[48] Therefore, low electric resistivity and higher deposit thickness can be expected for composite materials based on RuO_2. Results of this work indicate that thick RuO_2–TiO_2 films can be obtained.

As pointed out in Refs. 1–3, the production of OH^- increases the local pH, resulting in the precipitation of hydroxides or peroxides. However, according to Ref. 49 the peroxy-based route is completely different from deposition by a local pH increase. It was suggested[49] that in this case a pH increase is detrimental to deposition. At this point it is important to mention that addition of alkali to peroxy–titanate solutions results in precipitation of a peroxotitanium hydrate.[36] Therefore, the precipitation

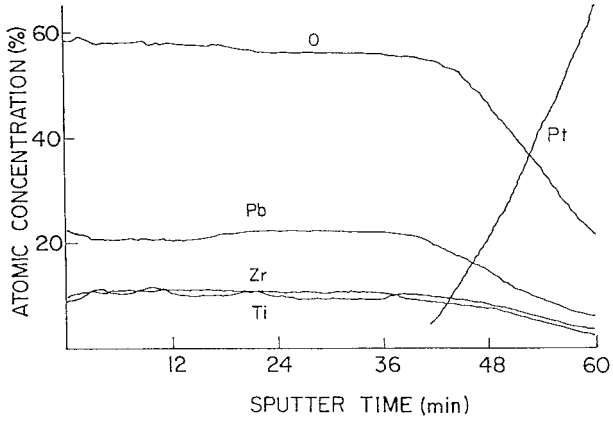

Fig. 7. Auger depth profile of PZT film on platinized silicon.

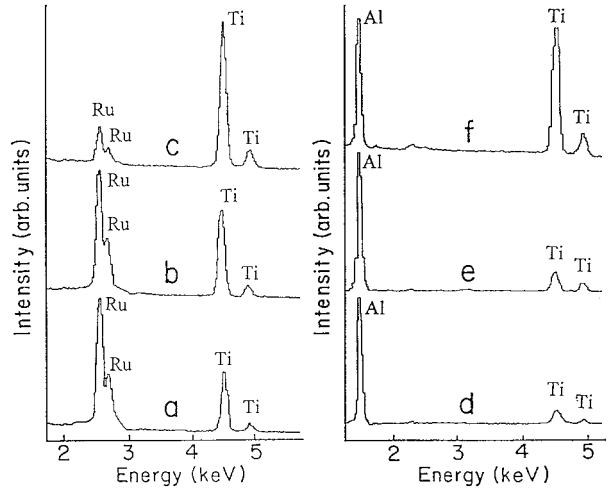

Fig. 8. EDS spectra for deposits obtained from stock solutions (a) 4, (b) 5, (c) 6, (d) 7, (e) 8, (f) 9.

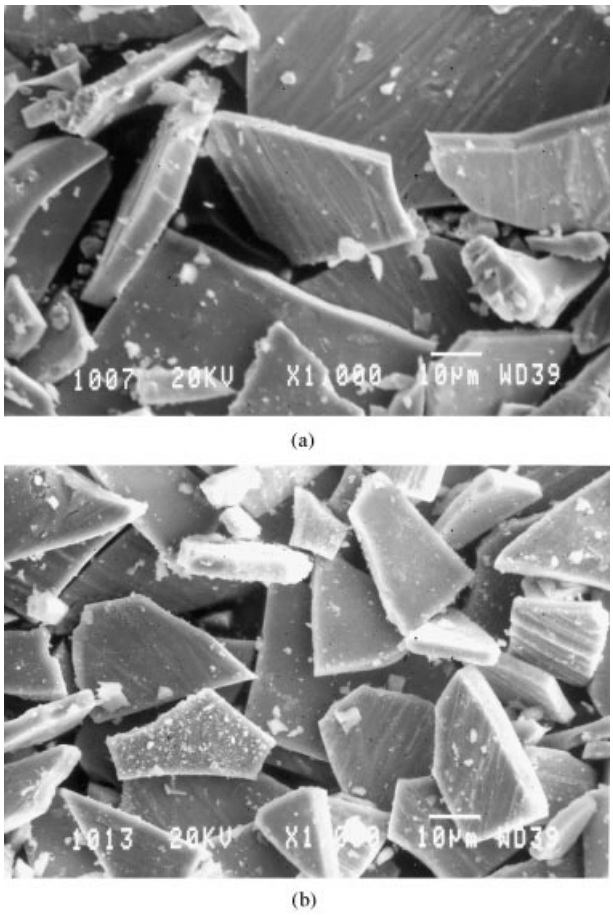

Fig. 9. SEM pictures of deposits (a) 5 and (b) 6 removed from Pt substrates and thermally treated at 600°C for 1 h.

of a peroxotitanium hydrate by electrogenerated base can also be expected.[2] Electrodeposition of titania is achieved via a peroxoprecursor.[2] As pointed out above, the peroxoprecursor method cannot be applied for deposition of RuO_2, as Ru species bring about decomposition of free H_2O_2 in solutions. The mechanism underlying the deposition of RuO_2 is based on a local pH increase.[17] Results of this work show that electrodeposition of Ti and electrodeposition of Ru species can be achieved simultaneously. Therefore it may be suggested that both processes are based on a local pH increase.

4 Conclusions

Hydrogen peroxide was utilized to stabilize Ti and Nb species in aqueous solutions and cathodic electrosynthesis of TiO_2 and Nb_2O_5 films and powders via the corresponding peroxoprecursors has been performed. Crystallization of titania (anatase) was observed at temperatures exceeding 400°C. Metastable pseudohexagonal Nb_2O_5 phase crystallized at 600°C, on further heating transformation to orthorhombic form (850°C) and monoclinic form (1200°C) was observed. Hydrogen peroxide decreases Cl^- concentration in solutions, however the residual Cl^- concentration in titania films was found to be in the range 0·06–0·09 at%. Electrodeposition of PZT films via the peroxoprecursor method was performed on platinized silicon wafers. The peroxoprecursor method developed for titania electrodeposition was utilized for electrodeposition of composite RuO_2–TiO_2 and Al_2O_3–TiO_2 materials of various compositions. Obtained results pave the way for electrodeposition of other oxides, complex titanates, niobates and composite materials.

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