Preparation of PZT Thin Films on Stainless Steel Using Electrochemical Reduction

Michio Koinuma, Hideki Ohmura, Yoshiro Fujioka, and Yasumichi Matsumoto[1]

Department of Applied Chemistry, Faculty of Engineering, Kumamoto University, 2-39-1, Kurokami, Kumamoto 860-0862, Japan

and

Satoshi Yamada

Department of Materials Science and Engineering, School of Science and Engineering, Teikyo University, 1-1, Toyosatodai, Utsunomiya 320-0003, Japan

PZT perovskite films which were strongly adhered to stainless steel were prepared by electrochemical reduction in solutions containing TiO^{2+}, ZrO^{2+}, and Pb^{2+} ions. The composition of the PZT films was easily controlled by the composition in the solution and the applied cathodic potential during the electrolysis. Heat treatment at 600 °C was necessary for crystallization, because the as-deposited oxide films were amorphous. Pb was deposited as a metal, while Zr and Ti were deposited as oxides and/or hydroxides during the electrolysis. The average of the dielectric constants of the PZT films prepared by the present method was more than 500. © 1998 Academic Press

INTRODUCTION

Some thin oxide films have usually been fabricated by various techniques such as evaporation (1), RF sputtering (2), laser ablation (3, 4), and metallo-organic chemical vapor deposition (5, 6). However, the preparation method for the oxide films using electrochemical deposition from aqueous solutions has several advantages compared with the above alternative coating techniques: the thickness and the composition of the deposit can be controlled by the electrochemical parameters; relatively uniform deposits are obtainable on complex shapes; the deposition rate is higher than that for other methods; and the apparatus is of low cost. $BaTiO_3/Ti$ (7), $LaMnO_3$ (8), and $LaCoO_3$ (9) have been prepared by electrochemical oxidation, and $LaCrO_3/$ (10), $BaTiO_3/$ (11), and PZT ($PbZr_{1-x}Ti_xO_3$)/stainless steels (12) have been prepared by electrochemical reduction.

PZT has been of considerable interest to the electronic industries, because of its dielectric and piezoelectric characterization. In the electrochemical reduction method, the pH increased at the electrode surface due to the consumption of H^+ and/or the production of OH^- ions accompanied by H absorption, adsorption, and/or H_2 evolution. In our previous paper (12), a preparation method for PZT films on stainless steel using electrochemical reduction in solutions containing $TiCl_3$, $ZrO(NO_3)_2$, and $Pb(NO_3)_2$ was described. However, these PZT films had shortcomings of adhesion to the substrates and the morphologies. This paper presents an electrochemical preparation method for PZT films which have strong adhesion to the stainless steel and thier morphologies and dielectric characterization.
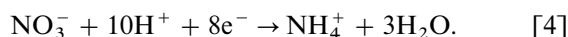
EXPERIMENTAL

A stainless steel (SUS-304: Ni 8–11 %, Cr 18–20 %) was used as the working electrode. Prior to each experiment, the working electrodes were sonicated in acetone for 5 min. A Pt plate and an Ag/AgCl (sat. KCl) electrode were used as the counter electrode and the reference electrode, respectively. The electrolyte was mixed with $Pb(NO_3)_2$, $ZrO(NO_3)_2 \cdot 2H_2O$, and $(NH_4)_2TiO(C_2O_4)_2 \cdot 2H_2O$ and was made up to a volume of 15 or 100 ml. The pH of the electrolyte solution was adjusted to 0.9 with 0.1M HNO_3 solution. The typical deposition time was about 10 min and the typical applied voltage was -3.0 V. All the samples were heated in air at various temperatures for crystallization, because the as-deposited oxide films were always amorphous. The structure of the oxide films before and after the heat treatment was examined by X-ray diffraction (XRD) analysis using monochromatic Cu$K\alpha$ radiation and scanning electron microscopy (SEM). The oxide films were dissolved in concentrated HCl and then analyzed by

[1]To whom correspondence should be addressed (fax: + 81-96-342-3659; E-mail: yasumi@gpo.kumamoto-u.ac.jp).

inductively coupled plasma (ICP) spectroscopy to determine the amounts of Pb, Zr, and Ti in the oxide films. Dielectric properties were measured using a frequency analyzer with an oscillation voltage of 50 mV and a frequency range of 10–20 kHz.
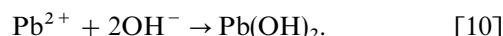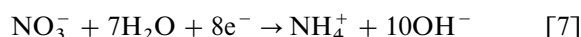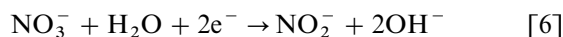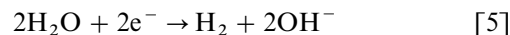
RESULTS AND DISCUSSION

Figure 1 shows the Pb/(Zr + Ti) atomic ratio in the as-deposited films prepared under potentiostatic electrolysis as a function of the applied potential. The electrolyte solution was a mixture of 0.0025 M $Pb(NO_3)_2$, 0.00125 M $ZrO(NO_3)_2 \cdot 2H_2O$, and 0.00125 M $(NH_4)_2TiO(C_2O_4)_2 \cdot 2H_2O$. The Zr/Ti atomic ratio was about 1 for all the as-deposited films. When the electrode potential was kept at -1.5 V during the electrolysis, the Pb/(Zr + Ti) atomic ratio was much larger than 1. In the present potential region, Pb metal deposition and the following electrochemical reactions proceeded:

$$H^+ + e^- \rightarrow H(ad) \text{ or } H(abs) \qquad [1]$$

$$2H^+ + 2e^- \rightarrow H_2 \qquad [2]$$

$$NO_3^- + 2H^+ + 2e^- \rightarrow NO_2^- + H_2O \qquad [3]$$

$$NO_3^- + 10H^+ + 8e^- \rightarrow NH_4^+ + 3H_2O. \qquad [4]$$

TiO_2 and $Zr(OH)_4$ deposition began to occur because reactions [1]–[4] consume H^+ and increase the pH at the electrode surface. However, only a small amount of TiO_2 and $Zr(OH)_4$ was formed in the vicinity of the electrode and

Pb metal deposition occurred predominantly. The PZT precursors prepared at a small overpotential had an excess of Pb atoms compared with the stoichiometric atomic ratio of Pb/(Zr + Ti). In a high overpotential region, H_2O is consumed to produce OH^- ion as follows (13):

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad [5]$$

$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^- \qquad [6]$$

$$NO_3^- + 7H_2O + 8e^- \rightarrow NH_4^+ + 10OH^- \qquad [7]$$

$$TiO^{2+} + 2OH^- \rightarrow TiO_2 + H_2O \qquad [8]$$

$$ZrO^{2+} + H_2O + 2OH^- \rightarrow Zr(OH)_4 \qquad [9]$$

$$Pb^{2+} + 2OH^- \rightarrow Pb(OH)_2. \qquad [10]$$

When the pH was increased in the vicinity of the electrode due to the production of OH^- ion, the formation of TiO_2 and $Zr(OH)_4$ as shown in reactions [8]–[9] actively proceeded, resulting in the PZT precursor whose Pb/(Zr + Ti) atomic ratio is close to 1. When a number of OH^- ions was produced by the electrochemical reduction, $Pb(OH)_2$ deposition gradually began to occur because the solubility product constant of $Pb(OH)_2$ is much smaller than those of $Zr(OH)_4$ and TiO_2. The codeposition of Pb metal, $Pb(OH)_2$, $Zr(OH)_4$, and TiO_2 occurred over a high overpotential region, and therefore, the Pb/(Zr + Ti) atomic ratio was increased again.

Figure 2 shows the Pb/(Zr + Ti) atomic ratio in the deposited oxide film prepared at -3.0 V as a function of
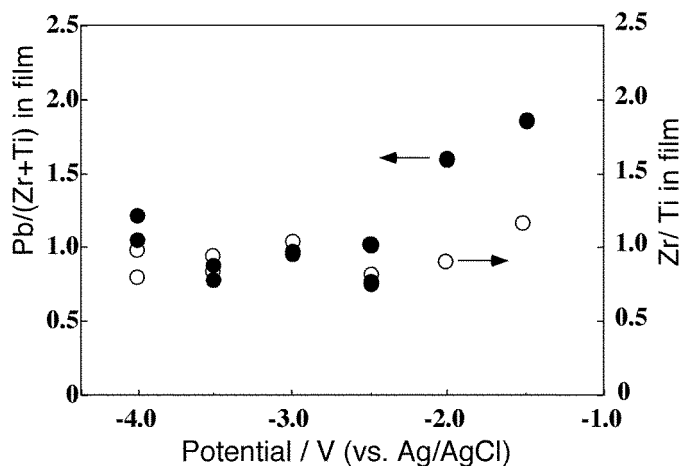

FIG. 1. Pb/(Zr + Ti) (●) and Zr/Ti (○) atomic ratios in the potentiostatically deposited film in a mixed solution consisting of 0.0025 M $Pb(NO_3)_2$, 0.00125 M $ZrO(NO_3)_2 \cdot 2H_2O$, and 0.00125 M $(NH_4)_2TiO(C_2O_4)_2 \cdot 2H_2O$ as a function of the applied potential. The volume of the solution is 15 ml.
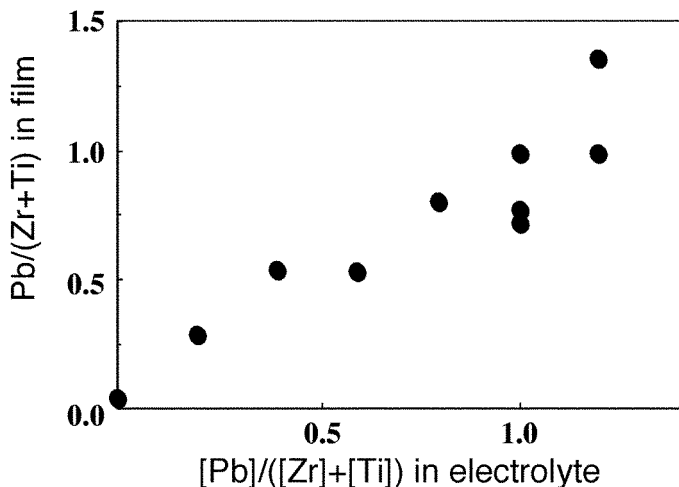

FIG. 2. Pb/(Zr + Ti) atomic ratio in the deposited film prepared at -3.0 V as a function of $[Pb^{2+}]/([ZrO^{2+}] + [TiO^{2+}])$ ratio in the solution where $[Pb^{2+}]$ is 0.01 M, and $[ZrO^{2+}]$ and $[TiO^{2+}]$ are changed from 0.0005 to 0.01 M and the volume is 15 ml.

the $[Pb^{2+}]/([ZrO^{2+}] + [TiO^{2+}])$ ratio in the solution, where $[Pb^{2+}]$ is 0.01 M and $[ZrO^{2+}]$ and $[TiO^{2+}]$ are changed from 0.0005 to 0.01 M. The volume of the electrolyte is 15 ml. When the $[ZrO^{2+}]$ and $[TiO^{2+}]$ were decreased in the electrolyte, the Pb/(Zr + Ti) atomic ratio in the film was also increased linearly. The Pb/(Zr + Ti) atomic ratios in the deposited oxide films are almost the same as those in the solution regardless of the $[ZrO^{2+}]/[TiO^{2+}]$ ratio. This result indicates that the composition of the deposited oxide film can be easily controlled by the composition of the solution.

Although the Pb/(Zr + Ti) atomic ratios in the films are almost the same as the $[Pb^{2+}]/([ZrO^{2+}] + [TiO^{2+}])$ ratio under these experimental conditions, the amount of Pb in the oxide films increases with the volume of the solution. Figure 3 shows the Pb/(Zr + Ti) atomic ratio where the volume of the solution is 100 ml and other conditions are the same as those in Fig. 2. The Pb/(Zr + Ti) atomic ratios in 100 ml are about twice those in 15 ml. The PbO_2 deposition from Pb^{2+} in the solution always proceeded on the counter electrode during the electrolysis. This deposition reaction results in the decrease in the $[Pb^{2+}]/([ZrO^{2+}] + [TiO^{2+}])$ ratio in the solution during the electrolysis. The amount of the deposited Pb on the substrate was greatly influenced by the volume of the solution. If the volume of the solution is small, the decrease in the $[Pb^{2+}]/([ZrO^{2+}] + [TiO^{2+}])$ ratio takes place drastically and consequently, and Pb deposition hardly occurs on the substrate. The formation of TiO_2 and $Zr(OH)_4$ proceeds preferentially in the later electrolysis, and the Pb/(Zr + Ti) atomic ratio of the precursor was close to 1.

Figures 4(a) and (b) show the X-ray diffraction patterns of the PZT precursor films on the stainless steel substrate after
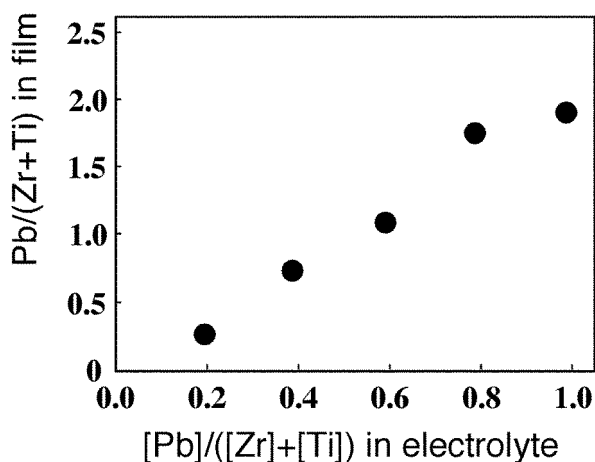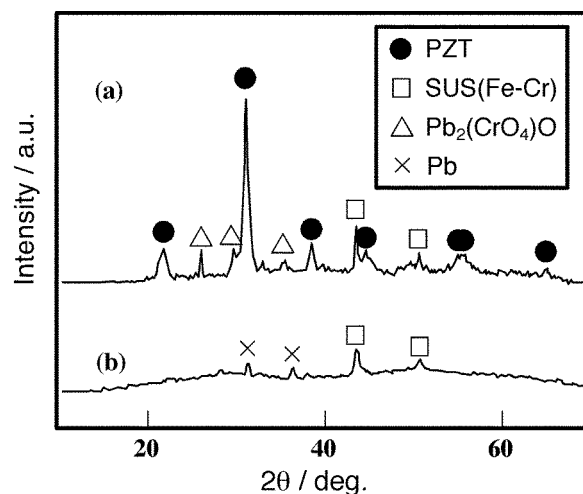

FIG. 4. XRD patterns of the PZT precursor film on the stainless steel substrate heated at 600°C (a) and the as-deposited PZT precursor film (b). The PZT precursors were prepared at -3.0 V for 10 min in a solution of 15 ml containing 0.025 M $[Pb^{2+}]$, 0.0125 M $[ZrO^{2+}]$ and 0.0125 M $[TiO^{2+}]$.

and before heat treatment at 600 °C for 3 h, respectively. The precursors were prepared at -3.0 V for 10 min in a solution of 15 ml containing 0.025 M $[Pb^{2+}]$, 0.0125 M $[ZrO^{2+}]$, and 0.0125 M $[TiO^{2+}]$. The XRD pattern of the PZT precursor film without heat treatment showed the peaks corresponding to Pb metal and the stainless steel substrate. This result suggests that Pb^{2+} ion in the solution is deposited on the substrate as a metal during the electrolysis. Moreover, the XRD pattern shows that the TiO_2 and $Zr(OH)_4$ in the PZT precursor film prepared during the electrolysis were amorphous. In the case of the PZT precursor film treated at 600 °C, many diffraction peaks derived from the PZT film appeared. The PZT precursor films were crystallized by heat treatment. Although these diffraction peaks were mainly related to the PZT perovskite, some peaks corresponding to impurities were observed.

Figure 5 shows an XRD pattern of the PZT precursor film on the Pt substrate after heat treatment at 600 °C. With the Pt substrate, the diffraction peaks indicated only the presence of the PZT perovskite and the Pt substrate. The impurities observed with the stainless substrate may be $Pb_2(CrO_4)O$ which formed in the reaction of the Pb metal and Cr in the stainless steel substrate because a large amount of Pb deposited at the interface. The temperature producing the PZT perovskite is lower than that of conventional ceramic techniques (> 1000 °C) and comparable to that in sol-gel thin film techniques (14).

Figures 6(a) and (b) show SEM photographs of the as-deposited PZT precursor film and the PZT precursor film after heat treatment at 600 °C. The as-deposited PZT precursor film has a mesh structure. The heat treatment
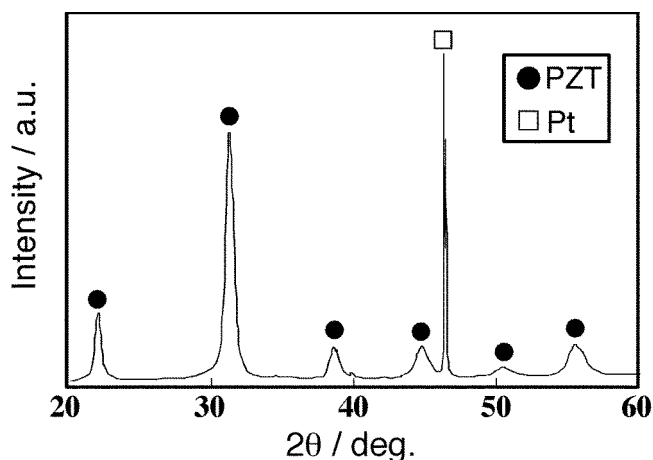

FIG. 3. Pb/(Zr + Ti) atomic ratio in the deposited film prepared at -3.0 V as a function of the $[Pb^{2+}]/([ZrO^{2+}] + [TiO^{2+}])$ ratio. Solution composition is the same as that in Fig. 2. The volume of the solution is 100 ml.

FIG. 5. XRD patterns of the PZT thin film on the Pt substrate after heat treatment at 600°C. Electrolysis condition is the same as that in Fig. 4.
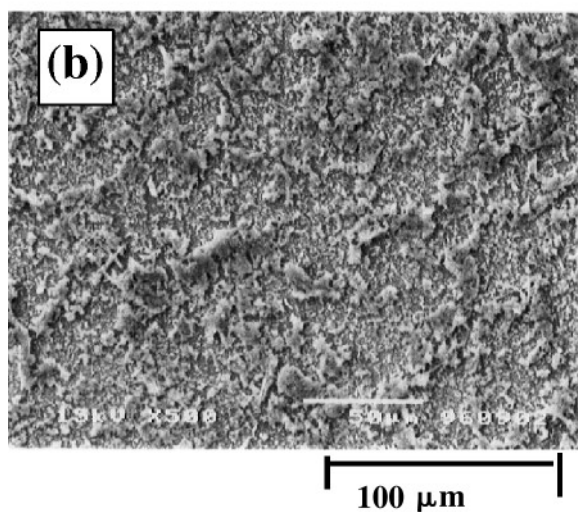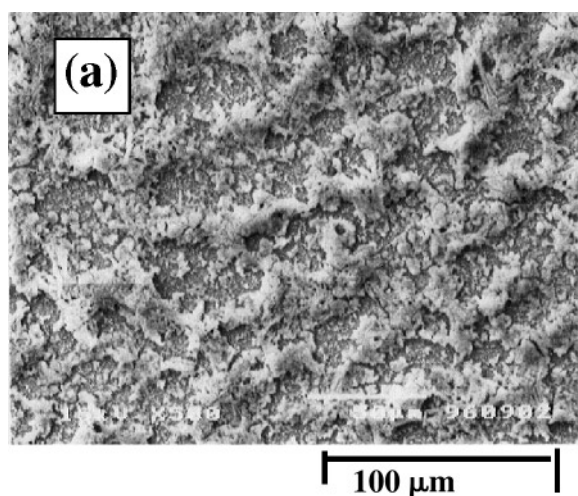

FIG. 6. SEM photographs of the as-deposited PZT precursor film (a) and the PZT precursor film heated at 600°C (b). Electrolysis condition is the same as that in Fig. 4.

shortens the width of the mesh and flattens the surface morphology. According to the EPMA results, a portion of the mesh structure consisted of a mixture of Ti and Zr oxides. From all the results, we assume that the PZT precursor films have a dual layer. The layer closest to the substrate may contain the metal Pb and outer layer may consist of a mixture of TiO_2 and $Zr(OH)_4$. TiO_2 and $Zr(OH)_4$ did not remain on the substrates because of the low adhesion, and therefore, Pb was mainly deposited on the substrate at the initial stage of the electrolysis. As the electrolysis proceeded, the Pb deposits on the substrate grew larger and became dendritic. TiO_2 and $Zr(OH)_4$ produced by the electrochemical reduction from the solution became incorporated into the dendritic structure of Pb. The dual layer was mixed and crystallized during the heat treatment, and therefore, the PZT thin films were formed on the substrates.

Figure 7 shows a typical SEM cross-sectional photograph obtained from the PZT film annealed for 3 h at 600 °C. From the cross-sectional photograph, the thickness of the PZT film was about 5 μm and there was no space between the PZT film and the substrate. Thus, the PZT film was adhered to the substrate and could not be peeled off by striking the substrate. The dielectric constant (ε), estimated using the film thickness obtained from the SEM photograph, was over 500 at room temperature, which was not different from the values of the films produced by other techniques, e.g., hydrothermal method ($\varepsilon = 640$) (15) and the sol-gel method ($\varepsilon = 376$) (16). This result suggests that the dielectric characteristics are not affected by the presence of $Pb_2(CrO_4)O$ at the interface.
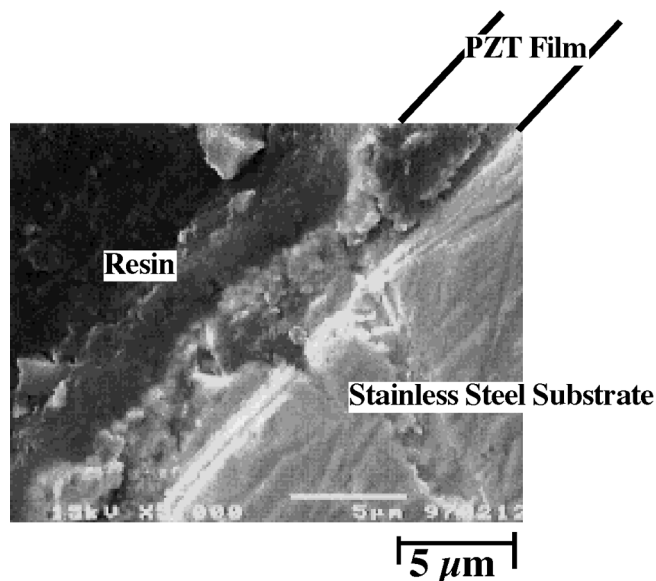

FIG. 7. A cross-sectional SEM photograph of the PZT film annealed at 600°C. Electrolysis condition is the same as that in Fig. 4.

CONCLUSIONS

The PZT thin film was prepared by the electrolysis of solutions containing $Pb(NO_3)_2$, $ZrO(NO_3)_2 \cdot 2H_2O$, and $(NH_4)_2TiO(C_2O_4)_2 \cdot 2H_2O$ under potential control. The PZT thin film has strong adhesion to the substrate. The $Pb/(Zr + Ti)$ atomic ratio in the film was adjusted by changing the electrolysis potential, the concentration of the electrolyte, and the volume of the electrolyte. When the electrolyte concentration was chosen as 0.0025 M $Pb(NO_3)_2$, 0.00125 M $ZrO(NO_3)_2 \cdot 2H_2O$, and 0.00125 M $(NH_4)_2TiO(C_2O_4)_2 \cdot 2H_2O$ and the volume as 15 ml, the expected atomic ratio of the PZT precursor was obtained using an applied potential of -3.0 V for 10 min. The PZT precursor became a PZT thin film with a dielectric constant of over 500 by heat treatment at temperatures higher than $600°C$.

ACKNOWLEDGMENTS

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