PREPARATION OF SOL-GEL THIN FILMS
BY ELECTROPHORETIC DEPOSITION

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ABSTRACT
Thin films of ZrO₂, Ta₂O₅, and lead zirconate-titanate, PZT, about 100 nm to 1000 nm in thickness, were prepared by electrophoretic deposition from transparent sols obtained by hydrolysis of metal alkoxides. Stainless steel plates and Pt-coated glass plates were used as substrates/electrodes. The constant voltage method was employed. The applied field was up to 20 V/cm. Thickness and refractive indices measurements were made by ellipsometry. The refractive indices of as-dried films were high. Uniformity of the chemical composition of PZT films, determined by electron probe microanalysis, EPMA, and Auger electron spectroscopy, AES, was better than the dip-coated PZT films. Effects of deposition conditions on physical properties of the films were discussed.

INTRODUCTION
The sol-gel method is known to be one of the most appropriate technologies to prepare functional oxide films. Many works on the preparation of sol-gel thin films by dip-coating and spin-coating have been published. Theoretical analysis of dip-coating and spin-coating processes have been also reported. However, few works on electrophoretic deposition of sol-gel films have been reported. Dense and uniform coatings may be obtained by this method. Although substrates are restricted to conductive materials, it has potential to make dense, homogeneous, and pore-free films with interesting physical properties and applications such as microelectronics and integrated optics.

In this study, some oxide films, e.g. ZrO₂ for chemical and mechanical protective coating, Ta₂O₅ with high refractive index, and ferroelectric PZT, were prepared by electrophoretic deposition from sols obtained by hydrolysis.
of metal alkoxides in alcoholic solutions. The effects of deposition conditions on physical properties of the films were investigated as well as the deposition mechanism.

EXPERIMENTAL PROCEDURES

ZrO₂ sols were prepared by hydrolysis of Zr(O-C₄H₉)₄ in ethanol with HNO₃ catalyst at room temperature. The concentration of Zr(O-C₄H₉)₄ was 0.15 mol/l. The viscosity of the coating sol was about 2.5 cp with a pH of about 4.7.

Ta₂O₅ sols were prepared from Ta(O-C₂H₅)₅ by hydrolysis in ethanol solution with HCl catalyst at room temperature. The pH value of the sol was about 1.8.

PZT sols were prepared by hydrolysis of Pb(O-iso-C₃H₇)₂, Zr(O-C₄H₉)₄, and Ti(O-iso-C₃H₇)₄ in 1-propanol with acetylacetone at room temperature. The concentration, viscosity, and pH of sol was 0.15 mol/l as PZT, about 5 cp, and about 8.8, respectively.

Electrophoretic deposition was made at room temperature. The substrate was placed between two counter electrodes in order to make coatings on both surfaces of the substrate. Plates of stainless steel, SUS304, or Pt-coated glass plates were used as substrates/electrodes. The substrates were cleaned by acidic solution and acetone vapor, and dried. The electrode distance was 1 cm. The applied voltage was 1 to 20 V, and the constant voltage method was employed. Dip-coated films were prepared from the same sols, and the withdrawal rate was 5 to 12 cm/min.

After drying at room temperature for 24 h, the weight of deposited film was measured. The thickness and refractive index measurements were made for the as-dried films by ellipsometry (Shimadzu, AEP-100). The as-dried films, about 100 nm in thickness, were transparent and apparently crack-free. X-ray diffraction measurements were made using a rotating sample holder for thin films (Rigaku, 2651Al with RAD-C X-ray generator) after drying and heat treating. PZT films were dissolved into HNO₃ solution, and the chemical composition was determined by inductively coupled plasma mass spectrometry, ICP-MS (Yokogawa Electric Co., PMS2000). The distributions of chemical composition were also determined by EPMA (Shimadzu, EPMA-8705) in the direction parallel to the surface, and by AES (JEOL, JAMP-10SX) and Ar ion etching in the direction perpendicular to the film surface.

RESULTS AND DISCUSSION

ZrO₂

For ZrO₂ films deposited on the cathode, the value of pH of the coating solution, about 4.7, was lower than the isoelectric point, IEP, for ZrO₂ known to be 6.7. Therefore, positively charged ZrO₂ particles migrated to the cathode and deposited there.

The effects of the applied voltage on the current, the amount of deposited film, the thickness, and the refractive index of the films are shown in Figure 1. The amount of deposited films, w, increased with increasing applied voltage up to about 5 V, but the relationship between w and the