Synthesis of Titania Thin Films by Cathodic Electrolytic Deposition

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The cathodic electrodeposition of titania thin films from solutions containing a titanium salt was studied. Titanium tetrachloride was dissolved in an ethanol-water solution with hydrogen peroxide to prepare titanium peroxocomplex solutions. The deposition of the titania precursor on platinum-coated silicon wafer substrates was carried out by electrolysis of the solutions under constant current conditions. The deposits were thermally treated at fixed temperatures in air and then characterized by X-ray diffraction and scanning electron microscopy.

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1. Introduction

Electrochemical methods are increasingly being used for the preparation of thin films and the coatings of ceramic materials. Electrodeposition, which has been developed as a metal-coating technique, is also being recognized as an effective technique for the preparation of ceramic films. The electrodeposition includes two commonly-used processing techniques; i.e., the electrophoretic deposition (EPD) which utilizes the colloidal suspension of ceramic particles, \(^{1–3}\) and the electrolytic deposition (ELD) which starts from a solution of metal salts. \(^{4–7}\) The EPD is achieved via electrophoresis of surface-charged particles dispersed in a liquid towards an electrode under an applied electric field. The deposit formation on the electrode is achieved via particle coagulation. ELD produces thin ceramic films from salt solutions by the production of metal oxides or hydroxides in electrode reactions. Cathodic ELD is a relatively new technique in ceramic processing. During the process, various reactions, which are often called cathodic reactions, could cause a local pH increase or generate OH\(^–\) groups at the cathode. Some of possible reactions are as follows: \(^{8}\)

\[
\begin{align*}
2\text{H}_2\text{O} + 2\text{e}^- &\rightarrow \text{H}_2 + 2\text{OH}^- \\
\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- &\rightarrow 4\text{OH}^- \\
\text{NO}_3^- + \text{H}_2\text{O} + 2\text{e}^- &\rightarrow \text{NO}_2^- + 2\text{OH}^- \\
\text{M}^+ + \text{OH}^- &\rightarrow \text{MOH}
\end{align*}
\]

Metal ions or complexes migrated to the cathode are hydrolyzed by electrogernated base to form oxide, hydroxide or peroxide deposits on the cathodic substrates:

2. Experimental

3 mM titanium (IV) chloride was dissolved in an ethanol-water (3:1) solution with cooling in an ice-water bath, and then 10 mM hydrogen peroxide (30 mass% in water) was added with stirring to prepare a yellow, transparent titanium peroxocomplex solution. The pH of the solution was in the range of 1.1–1.3. \(^{10}\) The electrolytic deposition of the solution was carried out at a constant current density of 5 mA/cm\(^2\) using a galvanostat. A Pt coated Si wafer and Pt plate were used as the cathodic substrates and the counter electrodes, respectively. The distance between the two electrodes was fixed at 10 mm with the working area of 10\(\times\)10 mm\(^2\). The titanium peroxocomplex solution was cooled in the ice-water bath during the ELD. The deposited layers were dried in air and then thermally treated at fixed temperatures. The identification of the layers was conducted by thin-film X-ray diffraction. The microstructures of the layers were observed using a scanning electron microscope (SEM) or an atomic force microscope (AFM).

3. Results and discussion

Thin deposit layers were obtained by applying an electric field between the electrodes while no deposit was formed by merely dipping the substrate in the solution. An SEM micrograph of the as-deposited layer prepared by the ELD for 20 min is shown in Fig. 1. The layer has the thickness of 100 nm, a uniform surface structure, and no cracks and exfoliation. The good adhesion of the layer to the substrate was confirmed by the Scotch tape peel test. The deposition at a high current density for a longer time could produce thicker deposits, but most of these deposits crumbled during drying and easily removed from the substrate. The change in the XRD pattern of the deposit while heating is shown in Fig. 2. No obvious diffraction peaks are detected for the as-deposited layer probably due to the inferior crystallization property. The anatase phase peak appears by heating the precursor deposit at 400°C and its intensity increases by heating at 700°C. This anatase peak disappears by heating at 1000°C, while the peak for the rutile phase then appears. The SEM micrograph of the anatase film deposited by the ELD followed by heating at 700°C is
When the electric current is applied to the solution, the local pH increase and the OH⁻ generation occurs at the cathode. The titanium peroxocomplexes migrate to the cathode and then they are hydrolyzed to form the deposition layer of titanium hydroxide.

\[
\begin{align*}
\text{TiCl}_4 &\rightarrow \text{Ti}^{4+} + 4\text{Cl}^- \\
\text{Ti}^{4+} + \text{H}_2\text{O}_2 + (n-2)\text{H}_2\text{O} &\rightarrow [\text{Ti(O}_2\text{)}(\text{OH})_{n-2}]^{4-} + n\text{H}^+ \\
+k\text{H}_2\text{O} &\rightarrow \text{TiO}_3(\text{H}_2\text{O})_x \\
\end{align*}
\]

The titanium hydroxide decomposes to titanium dioxide by the subsequent thermal treatment.

\[
2\text{TiO}_3(\text{H}_2\text{O})_x \rightarrow 2\text{TiO}_2 + \text{O}_2 + 2x\text{H}_2\text{O}
\]

The titanium hydroxide seems to play an important role as a binder during the processing steps.

It was observed that the titanium peroxocomplex solution became cloudy when the used-solution was stirring for 3 d at room temperature. Figure 4 shows the transmission electron microscope (TEM) photograph of the cloud. The cloud consists of many fine particles smaller than 10 nm. An electron diffraction (ED) analysis revealed that the particles are not amorphous, but have a crystalline structure. Some ED rings were assigned to the anatase phase of titania, but the others could not be identified. Using the particle-suspended titanium peroxocomplex solution, the cathodic deposition was attempted again. An SEM micrograph of the as-deposited layer prepared by the ELD for 20 min is shown in Fig. 5. The layer has a thickness of 2 μm, which is much thicker than the film in Fig. 2. The increase in the deposition rate is probably due to the co-deposition of titanim hydroxide by the ELD and titania particles by the EPD. It was revealed by depth profiling using the AFM that some cracks on the surface of the film reached the substrate as shown in Fig. 6. Though there were innumerable cracks on the surface, the deposit also showed a good adhesion to the substrate. It is likely that the co-deposited hydroxide phase plays the role of binder and suppresses the exfoliation of the layer.\(^{15,16}\) The change in the XRD pattern of the deposit by heating is shown in Fig. 7. The deposit transforms from microcrystalline to anatase and then rutile depending on the heating temperature. The titania film after the thermal treatment also showed a good adhesion to the substrate.
4. Conclusions

The thin layer of the titania precursor was prepared from a titanium peroxocomplex solution by cathodic ELD. The anatase film with a good uniformity and excellent adhesion to the substrate was obtained by the thermal treatment of the precursor deposit layer at 700°C. It was difficult to prepare the titania thick deposits with no exfoliation by the ELD, but it could be possible by using the particle-suspended titanium peroxocomplex solution.

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References