Characterization of Layered Titanate Thin Films

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Received June 8, 1999 ; Accepted August 27, 1999

A layered titanate acid, $\text{Cs}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4$ ($x=0.67$, $\square$: vacancy), was exfoliated in ethylamine aqueous solution, and layered thin films were prepared on the substrate by spin-coating method. Tabular titanates of some hundreds nm were arranged in parallel with the substrate. Although ethylamine aqueous solution did not exfoliate into the monolayer sheets, exfoliation to 10-15 layers sheets was found to be possible. The thickness of the film could be roughly controlled by repetition of the spin-coating.

Key Words : Layered Titanate Thin Film, Exfoliation, Spin-coating

1 Introduction

The thin films which consist of inorganic compounds are utilized in various fields, and the manufacture methods are also manifold. For the application of materials as the electrode, the form or thin film would facilitate the electrochemical and morphological evaluations. Until now, electrochemical technique, CVD (chemical vapor deposition)¹⁾ and MBE (molecular beam epitaxy)²⁾ and so on were utilized as the manufacture methods of thin films. The equipment in these techniques is usually complicated, and the thin film preparation condition is not easily fixed. In addition, the proper arrangement of the layers in the structure of the layered metal oxides is difficult, as well as the production of thin films. Recently we reported the synthesis of a layered thin film by exfoliating particles of the layered metal oxide followed by spin-coating of the suspension on a substrate.³⁾ One of the advantages of this method is the facility of the lamination of the layered oxide without requiring the complicated equipment. In this paper, we report the layered thin films produced by taking advantage of the exfoliation⁴⁻⁷⁾ of layered titanate acid $\text{Cs}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4$ ($x=0.67$, $\square$: vacancy),⁷⁻¹⁰⁾ and the characterization of the thin films are described.

2 Experimental

Layered titanate acid, $\text{Cs}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4$ ($x=0.67$), was synthesized by mixing Cs_2CO_3 and TiO_2 at the stoichiometric ratio and calcination at 800 °C for 20 hours. The proton exchange of $\text{Cs}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4$ was carried out by stirring in 1 N hydrochloric acid aqueous solution at room temperature for 2 days. The layer exfoliation of $\text{H}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4$ was performed by stirring in ethylamine aqueous solution ($\text{H}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4$: ethylamine = 1 : 8) at room temperature for 24

hours. Then, the suspension was centrifugally separated at 1000 rpm for 30 minutes, and the supernatant which was not precipitated was used as a mother suspension. The formation of a thin film by spin-coating was carried out by the following procedures. The quartz substrate was fixed in the spin coater, and about 0.1 ml of the suspension was dropped using a pipette. The coated substrate was rotated at about 2000 rpm until the solution uniformly spread. A thin film was formed by repeating this process several times. The thin films were characterized by X-ray diffractometry (XRD, Geigerflex RAD-B system Cu K α 15 mA, Rigaku), scanning electron microscopy (SEM, HITACHI S-4700), transmission electron microscopy (TEM, JEM-2010F) and ellipsometry (Jasco M-150).

3 Results and Discussion

A SEM image of the surface of layered titanate thin film obtained by spin-coating is shown in Fig. 1. In this image, the crystal of the even and tabular titanate acid of several hundreds nm was observed, and they

Fig. 1 A SEM image of the surface of layered titanate thin film.

are considered to be arranged in parallel with the substrate. This fact is also indicated from the XRD pattern of the layered titanate thin film as shown in Fig. 2. Since only the diffraction peak which derives from the perpendicular *c*-axis for the layer was observed in Fig. 2, this thin film is regarded as forming layer structure. Therefore, the crystals of titanate acid of the thin film did not laminate randomly, but parallelly overlapped on the substrate. It is noted that the ethylamine exists in the interlayer space of this thin film.³⁾

A TEM image of the cross section of layered titanate thin film is shown in Fig. 3. In this image, it is evidenced that the fine particles of layered titanate acid of 10-15 nm thicknesses have parallelly piled up on the substrate. It is estimated that each fine particle is the assembly of about 10-15 layers of titanate sheet, because the interlayer distance of a thin film is estimated to be 0.96 nm from Fig. 2. From this result, layer exfoliation by the ethylamine aqueous solution is not complete to the monolayer, and the suspension is considered to contain fine particles of layered titanate with the 10-15 nm thicknesses with the ethylamine in the interlayer spaces. The layer exfoliation was also attempted by other amine solutions as well as the hydroxide tetrabutylammonium solution. However, although it was possible to insert the amine

in the interlayer space, the layer exfoliation did not occur. From these results, it is suggested that ethylamine is possible to weaken the interaction between the titanate sheets after intercalation and seems to have the ability for exfoliation at intervals.

Figure 4(a)-(c) shows TEM images of the cross section of layered titanate thin films in changing the number of spin-coating. The number of spin-coating is 1, 3 and 10 times for images (a), (b) and (c), respectively. The single spin-coating resulted in a thin film of about 20 nm in thickness, and it becomes about 100 and 300 nm in 3 and 10 times, respectively. It becomes clear that the film thickness can be roughly controlled by the times of spin-coating. The film thickness estimated by TEM was further confirmed by the measurement by an ellipsometry. The transparency of a

Fig. 2 The XRD pattern of layered titanate thin film.

Fig. 3 A TEM image of the cross section of layered titanate thin film.

(a)

(b)

(c)

Fig. 4 The TEM images of the cross section of layered titanate thin films in changing the frequency of the spin coat : a) 1 time ; b) 3 times ; c) 10 times.

thin film became poor when the thickness was increased.

4 Conclusion

A thin film which consisted of layered titanate was obtained by utilizing layer exfoliation using ethylamine aqueous solution. This thin film made by spin-coating did not randomly laminate but parallelly arranged the crystal of titanate on the substrate. The layer exfoliation by the ethylamine partially occurred, but not to a single layer. By changing the number of spin-coating, it was possible to control the film thickness to some extent.

Acknowledgment

This work was partially supported by Grant-in-Aid for Scientific Research on Priority Area of "Electrochemistry of Ordered Interfaces" (No. 09237225) and (A) (No. 10304060) from the Ministry of Education, Science, Sports and Culture, Japan and by Research for the future program (RFTF), The Japan Society for the Promotion of Science (JSPS) JSPS-RFTF 96R06901 and by CREST of JST (Japan Science and Technology) and by Tokuyama Science Foundation. We thank JEOL Ltd. for the help in obtaining the TEM photograph and are also grateful to HITACHI

Ltd. for obtaining the SEM photograph. We thank JASCO Ltd. for helping in measurement of the film thickness.

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