Physical Properties and Applications of Advanced Materials

Editor-in-Chief: **Shixun Cao**

Vice-Chief Editors: **Atsushi Saiki, Shujuan Yuan**

Shanghai University Press

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内容简介

作为第六届先进材料物性和应用国际学术研讨会的会议论文集，本书内容主要包括以下六个方面的最新研究进展：1）先进材料的制备和表征；2）先进功能材料的结构和物性；3）纳米结构材料物理与化学；4）自旋电子学、氧化物电子学与信息材料；5）超导材料的物理特性和应用；6）计算机辅助材料设计。

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Preface

Welcome to the 6th International Conference on the Physical Properties and Applications of Advanced Materials (ICPMAT-VI)! Based on the agreement between Shanghai University, China and the University of Toyama, Japan, signed in April 2006 by Prof. Qingyi Pan, Dean of the School for Sciences of Shanghai University, and Prof. Tokuso Saitou, the President of the University of Toyama, the first Sino-Nippon Cooperation Symposium on Superconductivity and Nanotechnology was held in Shanghai in Nov. 2006. Since then, the series of conferences have been held and expanded every year, and have been developed into the international conference today with participants from more than 10 different countries. The conference provides a platform for fruitful discussion, exchange, and cooperation among scientists, engineers, researchers as well as other related scholars in some selected disciplines and inter-disciplines of advanced materials.

The proceedings include recent progress relating to the physics, technology and applications of different functional materials such as superconductors(including Fe-based superconductors), oxides, metal alloys, ferroelectrics, spintronics and solar cells, as well as their novel nano-structures, selected from more than 100 papers presented at the conference and authored by many distinguished scholars. I believe that the proceedings will be very helpful for your study and research activities.

I would like to express my gratitude to the Natural Science Foundation of China; Shanghai University; the University of Toyama, Japan; the International Office of Shanghai University as well as Shanghai University Press for their support and contributions. I would also like to express my appreciation to my colleagues, Profs. Shixun Cao, Jincang Zhang, Peifeng Weng, and Wencong Lu, from the College of Sciences of Shanghai University as well as many collaborators from China and abroad, for their efforts.

Xuechu Shen
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Part I

Processing and Characterization for Advanced Materials

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CeO_2 Thin Films Grown on Glass Substrate from Aqueous Solution and Their Optical Property

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Abstract: In this study CeO_2 precursor thin films were deposited onto insulating glass substrates at a room temperature from an aqueous solution by applying constant electrical field and their optical properties were in researched. The precursor was the aqueous solution of $Ce(NO_3)_3$-$6H_2O$, and 8mol%$M(NO_3)_3$-$6H_2O$, (M=Y,Gd,Sm) and a little NH_3 aq.. The insulating glass substrate was placed on the minus carbon electrode. By applying electrical field, M-$Ce(OH)_3$ thin film was effectively deposited on glass substrates under the condition of the applied voltage of 2.6V~3.6V for 20min~30min at room temperature. The crystalline phase of M-CeO_2 thin films with a transparent and smooth surface can be obtained after annealing at 823 K for 5 h in air. Spectral transmission curves changed due to the film by an additive, and 10 to 30 % absorption peaks were observed around 310 to 330 nm in the visible to ultraviolet light region with the grown M-CeO_2 films.

Key words: CeO_2, thin film, electro-chemical depotision.

1. Introduction

Pure ceria (CeO_2) thin film have many attractive characteristics, such as ion conduction[1], oxygen storage[2], and high optical transparency in visible light region and interceptor property from ultraviolet region [3-5]. Therefore, CeO_2 film was applied to various fields. For example, silicon-on-insulator structures[6], electrolytes or electrodes in solid oxide fuel cells[7-10], oxygen sensor, UV light preventive glasses and smart window devices. For these applications CeO_2 film with a strong adhesion to a substrate and without structural defects are suitable[11].Many method have been prepared to prepare CeO_2 thin film, such as electrochemical vapour deposition or vacuum processes including magnetron sputtering, sol-gel[12], chemical solution techniques, have been reported to prepare CeO_2 thin and dense film.

The electoro-chemical deposition is much simpler and inexpensive and have several advantages, such as easily controllable deposition rate. In this method, since precipitation reaction occurred with assistance of the electriced field, they were influenced by the applied voltage. By applying a more negative bias than the hydrogen evolution potential of H_2O, the pH near the electrode surface raises , and then Ce^{3+} is precipitated as a hydroxide on the glass substrate surface. Naturally, the cathodic method is applicable to not only Ce^{3+}, but also other metal ions taking part in the precipitation at high pH and then Y^{3+} is also precipitate almost at the same time [13]. And a similar thing happens about Gd^{3+}, Sm^{3+}.The composition of the films was almost the same as with that of the aqueous solution.

In this study, metal (Y,Gd,Sm...etc.) doped CeO_2 precursor films were deposited onto insulating glass substrates at a room temperature from an aqueous solution by applying constant electrical field and their optical properties were investigated.

2. Experimental

CeO_2 thin films on insulating glass substrate by using electro-chemical deposition method using aqueous

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solution. Insulating glass substrates (9.0 mm×18 mm ×0.15 mm) were cleaned ultrasonically in a acetone and glass cleaner (Semicoclean56). After glass cleaned, UV irradiation was performed for 1h in insulating glass substrates UV irradiation was performed for 1 h.

The precursor was the aqueous solution of 92mol%$Ce(NO_3)_3$ - $6H_2O$, 8mol%$M(NO_3)_3$ - $6H_2O$, (M=Y,Gd,Sm...etc.) and a little NH_3 aq.. The precursor solution concentration was made 0.1mol/L. Appropriate quantities (0-5.0 vol%) of an ammonia aueous solution (NH_3(aq), 23%) were added to adjust the acidity and to promote a radical exchange reaction between the $Ce(NO_3)_3$ and NH_4OH to produce an intermediate product of $Ce(OH)_3$. After the mixture was stirred for 1h, a homogeneous colorless and transparent solution was obtained. The glass substrate was placed on the minus carbon electrode. The distance between the minus carbon electrode and glass substrate was set to be 96μm. By applying electrical field, thin film was effectively deposited on glass substrates under the condition of the applied voltage of 2.6 V-3.6 V for 20-60 minutes at room temperature. The as-deposited film was amorphous, and a crystalline phase of CeO_2 with a transparent and smooth surface can be obtained after annealing at 823K for 5 h in air.

The crystallization of the films was investigated using an X-ray diffractometer (XRD, 40kV, 30mA, CuKa, LabX, Shimadzu). The chemical compositions of the films were analysed by X-ray fluorescence spectrometer (PW2400, PANalytical). Morphology of the films was observed by scanning electron microscope (SEM, TM-1000, HITACHI), and optical microscope (BHSM-313MB,OLIMPUS). UV to visible light transmittance change were analysed by spectrophotometer (LAMBDA-950, PerkinElmer).

3. Results and discussion

3.1 CeO_2 film deposition

As-deposited films were relatively flat and transparent, when applied electrical field was between 2.6V-3.6V, but amorphous and no obvious diffraction peaks were detected. Therefore metal (Y,Gd,Sm) doped $Ce(OH)_3$ was changed into metal doped CeO_2 by oxidation and dehydration by the heat treatment at 823K for 5h.

Fig.1 showed the XRD patterns of the Y doped CeO_2 (Y-CeO_2) precursor solution deposited film by applying the voltage of 2.6 V - 3.6 V for 60min.The Y-CeO_2 films were obtained transparent and hardly crystallized. When the high voltage of the 3.4V-3.6V was applied, the intensity of diffraction peaks increased gradually. Fig.2 showed the optical micrographs of Y-CeO_2 film surfaces deposited by applying the voltage of 2.6 V to 3.6 V for 60minutes and heat treated. At low voltage was applied, deposition film had flat, colorless and transparent surface. When higher voltage was applied, the thicker or rough surface films were deposited in the same deposition time.

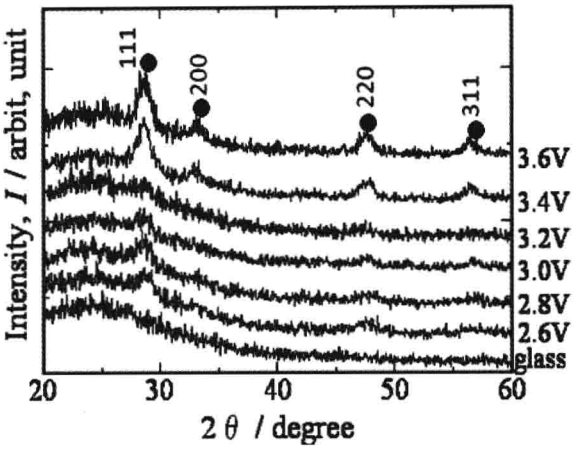

Fig.1 The XRD patterns of the Y-CeO_2 precursor films grown under the voltage of 2.6 V～3.6 V for 60 min

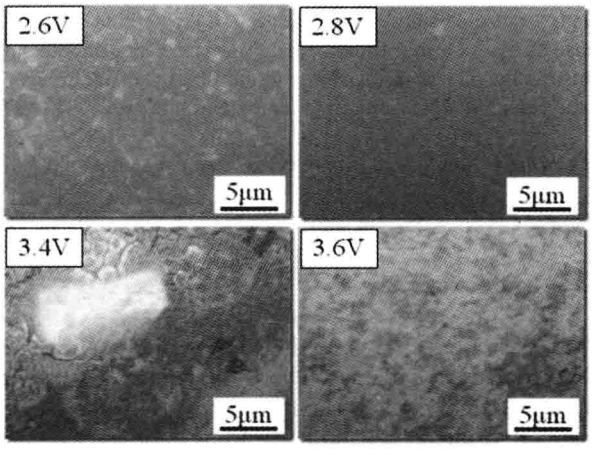

Fig.2 Optical micrographs of Y-CeO2 films deposited by applying the voltage of 2.6V to 3.6V for 60min

3.2 Film transmittance property and morphology

Fig.3 showed the spectral transmission curve of metal doped CeO_2 films. Well crystallized thin film had the transparent and smooth surface. Spectral transmission curves of Gd doped CeO_2 film, ultraviolet light was absorbed about 30 %. The absorbers of Gd doped CeO_2 was increased most. On the other hand, a peak of the absorption was different from other films in the Y-CeO_2 film, and the peak shifted to 310 nm. So, quantity of absorption may be controled and an absorption range of the Ultraviolet light of the CeO_2 film by the difference additives.