

Formation of cerium oxide thin films from aqueous solution

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The object of this study was to prepare cerium oxide thin films by homogeneous precipitation method. For this purpose a flow type equipment was prepared. A mixture of cerium nitrate and hexamethylenetetramine solutions was allowed to flow into this equipment. Reaction products were mainly deposited on a yttrium-doped zirconium oxide substrate. After the reaction, the products on the substrate were characterized by X-RD, SEM, etc. The products were in the form of thin film. X-ray diffraction analysis showed that the products were cerium oxide with some impurities.

Key words: cerium oxide, thin films, homogeneous precipitation, X-ray diffraction

1. INTRODUCTION

Cerium oxide is one of the rare earth element oxides with fluorite structure. Cerium oxide shows wide range of nonstoichiometry and is known to be a mixed conductor. As a result, cerium oxide is one of candidate materials for solid oxide fuel cell (SOFC) and is used as three way catalyst system in automobiles. Producing cerium oxide thin film would increase the application field of this material. General methods to deposit cerium oxide thin film are chemical vapor deposit (CVD),^[1] epitaxy,^[2] etc.^[3] Compared to these methods, preparation of oxide film from aqueous solution would have several advantages. In this method, energy consumption of the reaction is low, and materials including metals, ceramics and polymers can be used as the substrate regardless of their conductivity and melting point. And the preparation from aqueous solution is suitable for mass production. It was reported by Izaki et al.^[4] that the cerium oxide film was deposited chemically on a non-conductive glass substrate by simple immersion into aqueous solution containing hydrous cerium nitrate and dimethylamineborane (DMAB). The oxide film obtained in this way had a smooth surface and a high optical transmission.

In this method, the preparation of cerium oxide film was performed at temperature as low as 333 K.

The object of this study was to prepare cerium oxide thin films from cerium nitrate solution at low temperatures on the zirconium oxide (TPZ) substrate by homogeneous precipitation method. We used hexamethylenetetramine (HMT) as one of chemicals. We used this method because in homogeneous precipitation method the reaction rate can be controlled by adjusting the temperature of the solution.

2. EXPERIMENTAL PROCEDURE

A reaction of homogeneous precipitation method does not proceed at room temperature but proceeds at certain higher temperatures. Therefore, we can control the reaction by adjusting temperature of the solution. In this study, formation of cerium oxide thin film was tried by homogeneous precipitation method. To accomplish this objective, a flow type equipment was used, because the reaction could be confined in small region by flowing the reaction solution and heating it slowly and locally.

Y-doped zirconium oxide (TPZ) was polished and used as a substrate for the formation

of cerium oxide thin film. The polished substrate was washed by acetone and deionized water. After drying, a part of the substrate was covered by masking tape, and placed on the copper electrode in a cell. Volume of the cell was about 70 cm³. The reaction solution was a mixture of 0.05 M cerium nitrate solution and 1.0 M hexamethylenetetramine solution. The total quantity of the mixture was 500cm³. The equipment was filled up by this solution. Then the solution was circulated for 1 hour with several voltages applied between electrodes. Then the

equipment was heated up slowly, and the temperature in the equipment was kept at 85°C for 1 or 3 hours. Homogeneous precipitation reaction took place during this heating process. This process was carried out with two different electrode distances: 15 mm and 30 mm. After the reaction, the surface of the substrate was washed by deionized water, and the substrate was dried in air. The products on the substrate were characterized by the laser microscope, X-ray diffraction and etc.

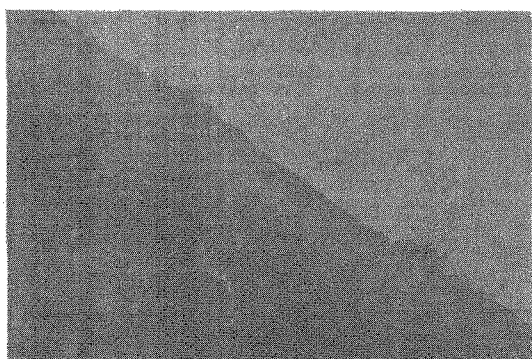


Fig 1-1(a)

20μm

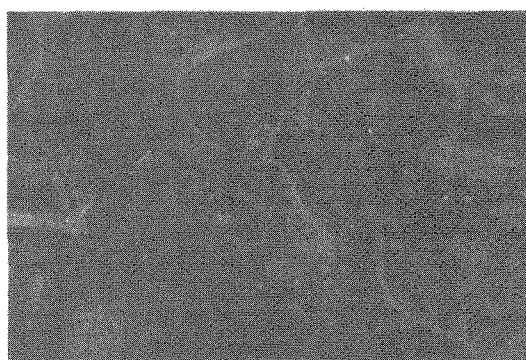


Fig 1-1(b)



Fig 1-2(a)

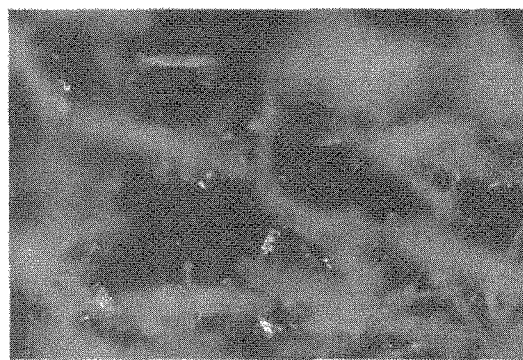


Fig 1-2(b)

Fig 1. The laser micrographs of the substrate surface after reaction: the distance of electrodes was 30 mm. Fig 1-1: the voltage was 70 mV. Fig 1-2: the voltage was 500 mV. (a): upper right corner of the area was covered with masking tape. (b): the area was not covered with masking tape

3. RESULTS AND DISCUSSION

Fig 1 shows a result of the laser microscope observation of a substrate surface after the reaction in the cell. Fig 1-1 and Fig 1-2 were the substrate surfaces after reaction: the voltage was 70 mV and 500 mV, respectively. The area on the

upper right hand side of Fig 1-1(a) and Fig 1-2(a) is the area where no reaction product is present because masking tape covered this area. The products were deposited as a thin film on the surface of substrate after reaction: the distance between electrodes was 30 mm. When voltage of

0 ~ 100 mV was applied between electrodes, the products in a form of a thin film were deposited. However, when the Voltage of 100 ~ 900 mV were applied, the products in a form of islands were partly deposited on the thin film deposition. Number of these island products increased as the voltage between electrodes increased. When the distance of electrodes was 15 mm, the repeated

experiments did not always produce the same deposition on the substrate. This was due to the fact that the flow of the reaction solution was not uniform when the distance between electrodes became short. Consequently fresh reaction solution did not always reach the vicinity of the substrate.

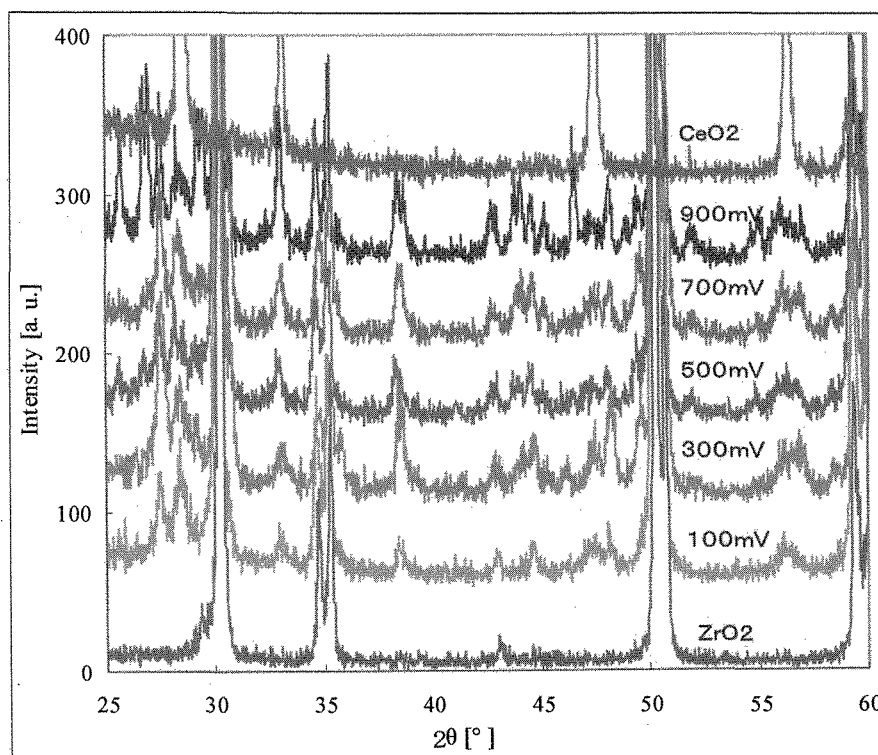
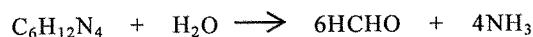


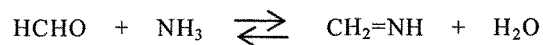
Fig 2. The X-RD results of the substrate before and after the reaction: the voltages are 100 ~ 900 mV. The results of ZrO₂ substrate and CeO₂ powder were included.

Fig 2 shows the X-RD results of the substrate after reaction. For comparison, X-RD result of substrate before the reaction is also shown. Although most of the peaks are those of substrate itself, the peaks of some products on the substrate were also observed. The peaks were those of cerium oxide. Therefore, it was confirmed that the product deposited on the substrate was cerium oxide. The intensity of the peaks was stronger when the voltage between electrodes increased. This indicates that the amount of the deposition depends on the voltage between electrodes. X-RD result shows that there

are some peaks other than ZrO₂ and CeO₂, indicating that some impurities were present in the product. Result of thermogravimetric analysis of cerium oxide revealed that the precipitate formed by homogeneous precipitation method using HMT contained some organic species. Therefore, these impurities found by X-RD might be related to organic species such as HCHO and CH₂=NH. They are the products of hydrolysis of hexamethylenetetramine^[5]:



and by-product of



5. CONCLUSIONS

Cerium oxide in a form of a thin film was obtained by homogeneous precipitation method with hexamethylenetetramine, and some impurities were included in the products. The voltage between electrodes influenced the precipitation process and consequently influenced the deposition products. The deposition products on the substrate were also affected by the distance between two electrodes.

6. REFERENCES

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