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FORMATION OF ZIRCONIUM TITANATE FROM MULTI-LAYERED STRUCTURE OF ZrO_2 AND TiO_2 DEPOSITED BY PULSED RAPID THERMAL CHEMICAL VAPOUR DEPOSITION

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ABSTRACT

PRTCVD (pulsed rapid thermal chemical vapor deposition) method has been introduced to prepare zirconium titanate ($ZrTiO_4$) films from a multi-layered structure composed of ZrO_2 and TiO_2 as a primitive oxide, which allows for the preparation of a given film with different element per cycle and precise control over the thickness of the film. The feasibility of PRTCVD was evaluated and it was confirmed that a multi-layered structure composed of different primitive oxides can be easily produced by PRTCVD and transformed into a multi-component single phase oxide such as zirconium titanate by an appropriate thermal annealing process.

KEY WORDS

PRTCVD, Zirconium titanate, Multi-layered structure, Thermal annealing

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INTRODUCTION

Zirconium titanate has been widely used in electrical and optical devices such as humidity sensors, capacitors, dielectric resonators, and composite materials [1-4]. Due to the dependence of physical properties of the material on stoichometry, exact controllability of stichiometry is critical for the successful applications. However, it is well known that the stoichiometric control of multi-component oxide films cannot be easily achieved when using the chemical vapor deposition (CVD) method [4]. To provide precise stoichiometric control during the application of CVD, PRTCVD (pulsed rapid thermal chemical vapor deposition) as a novel method was suggested.
In this work, the feasibility of PRTCVD was evaluated through the preparation of $ZrTiO_4$ films from a multilayer structure composed of ZrO_2 and TiO_2. The primitive oxides were deposited by PRTCVD alternatively followed by thermal annealing. The degree of crystalline $ZrTiO_4$ phase formed through solid interdiffusion was evaluated by TEM (transmission electron microscopy) and X-ray diffraction (XRD).

EXPERIMENTAL

P-type Si (100) wafer was used as a substrate. Metalorganic precursors of TiO_2 and ZrO_2 were TTIP (titanium tetra-isopropoxide, 5N) and ZTB (zirconium tetra-tert-butoxide, 4N), respectively. PRTCVD reactor was equipped with thermal components and a quartz tube with a 65 mm OD. Bubblers containing TTIP and ZTB were heated to 32℃ and 36℃, respectively, to equalize each vapor pressure. The vapors were carried into the reactor by nitrogen. The substrate temperature and reactor pressure were controlled at 350℃ and 500mTor, respectively. Oxygen of 30sccm was employed as a reaction gas and nitrogen carrying metalorganic vapors of 20sccm was supplied at a fixed value during the deposition of TiO_2 and ZrO_2. In PRTCVD, the cooling and heating pulsing is cycled for the film with different elements. The thickness of the film was controlled with deposition time at 350℃. A multi-layered structure of primitive oxides was prepared as follows: First, an initial oxide layer is deposited at a heating stage of 350℃ for a designated time. Second, all reactant species are eliminated by venting and simultaneously the substrate temperature is cooled to 300℃. Third, the substrate is heated to 350℃ for the deposition of the next oxide layer. One cycle in PRTCVD is composed of a combination of substrate heating, film deposition, and substrate cooling and reactant venting. After several cycles, a multi-layered structure with different oxide layers can be prepared by the PRTCVD method.

RESULTS AND DISCUSSION

Fig. 1 shows the schematic procedure of PRTCVD. At the deposition conditions given above, the deposition rate of ZrO_2 was 17nm/cycle and was faster than that of TiO_2 (10nm/cycle) at the same process conditions, where the deposition time per cycle was 30sec. ZTB has higher reactivity in terms of decomposition into the film than TTIP at the same temperature of 350℃ and vapor pressure, which leads to faster deposition of ZrO_2 than TiO_2. The molecular complexity of TTIP is 1.4 and that

of ZTB is 1.0. TTIP has a tendency to form more complex molecules than ZTB [5]. A previous study reported that Zr from ZTB was more easily incorporated into the deposited films than Ti from TTIP during PECVD of zirconium titanate [6]. Accordingly, additional process time for TiO_2 is needed to equalize the thickness of ZrO_2 and TiO_2.

A multi-layered structure of ZrO_2 and TiO_2 prepared by PRTCVD was inspected by TEM. Fig. 2(a) clearly shows an as-deposited multi-layered structure on a silicon substrate. The formation of a zirconium titanate film from the stacked layer of ZrO_2 and TiO_2 was performed by thermal annealing at 900℃ under nitrogen for 1hr. The image shown in Fig. 2(a) indicates that a multi-component oxide can be easily transformed from a multi-layered structure by an appropriate thermal annealing process. Through the XRD analysis, as-deposited TiO_2 and ZrO_2 at 350℃ showed an amorphous phase.

Fig. 3 shows the X-ray diffraction patterns of zirconium titanate with a composition of Zr/Ti=65/35 on Si substrates after being annealed at various temperatures under nitrogen for 30 min. At an annealing temperature of 700℃, peaks related to tetragonal and monoclinic ZrO_2 were detected; these peaks can be correlated with JCPDS files numbers 17-923 and 37-1484, respectively. However, above 900℃, peaks related to orthorhombic $ZrTiO_4$ were mainly detected [7]. This indicates that the transformation from a multi-layered structure to a multi-component single phase layer can occur at a temperature of just below 900℃ under nitrogen and the crystalline grain size would be increased with the annealing temperature.

Fig. 4 shows the effect of annealing time at a fixed temperature on the degree of crystallinity. The size of crystalline zirconium titanate increased with longer annealing time; the effect was comparable to the effect of annealing temperature.

Fig. 5 shows the results of XPS analysis of a multi-layered structure annealed at various temperatures. Two peaks of oxygen element at 500℃ annealing temperature were shown in Fig. 5(b), indicating that there are magnificently two kinds of combinations between oxygen and other elements; titanium and zirconium. As the annealing temperature increased, the two peaks of oxygen were merged into one peak.

The result implies that a multi-layered structure composed of TiO_2 and ZrO_2 is ready to be transformed into a single phase zirconium titanate by the increase of annealing temperature. According to the results from Fig. 3~5, the primary factor for the interdiffusion from a multi-layered multi-phase structure to a multi-component single phase structure could be considered as the annealing temperature rather than the annealing time, which is consistent with the previous report [8].

Further study will be made to explore the effect of the individual thickness of ZrO_2 and TiO_2 layers on the composition of the formed zirconium titanate to produce a more perfect film and the characteristics of zirconium titanate films with different ratios of Zr/Ti.

CONCLUSION

From the results, it was confirmed that a multi-layered structure composed of different primitive oxides can be easily produced by PRTCVD and transformed into a multi-component single phase oxide by an appropriate thermal annealing process. Therefore, the application of PRTCVD for multi-layered structures is a promising approach for realizing multi-component oxide thin films with high compositional controllability.

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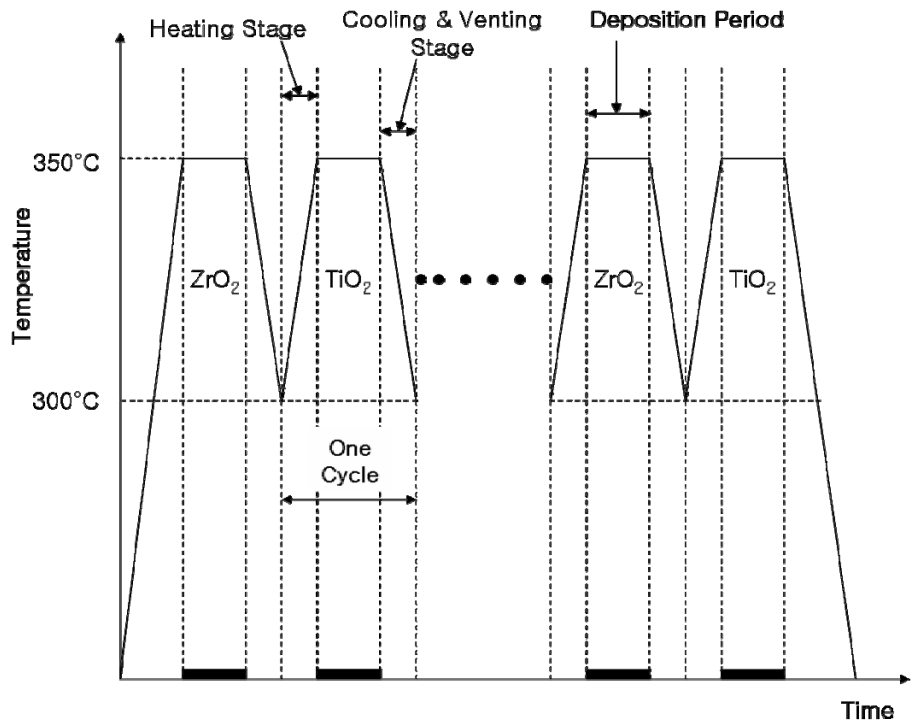

Fig.1. Process schematic of PRTCVD for multi-layered structure of ZrO_2 and TiO_2 thin film.

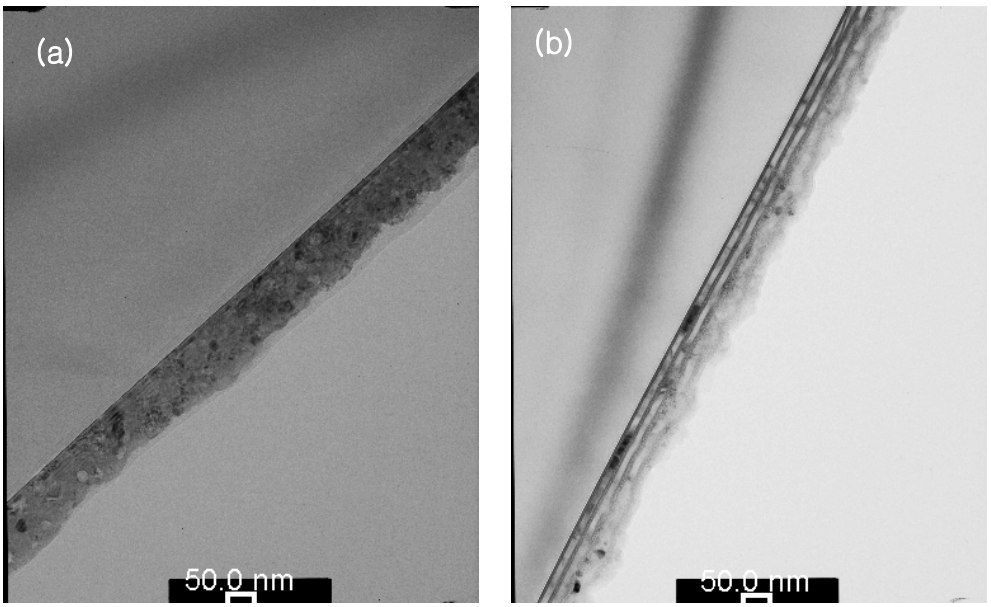

Fig.2. Cross sectional TEMs of (a) a multi-layered structure composed of as-deposited ZrO_2 and TiO_2 thin films and (b) the film annealed at 900℃ under nitrogen gas for 1hr.

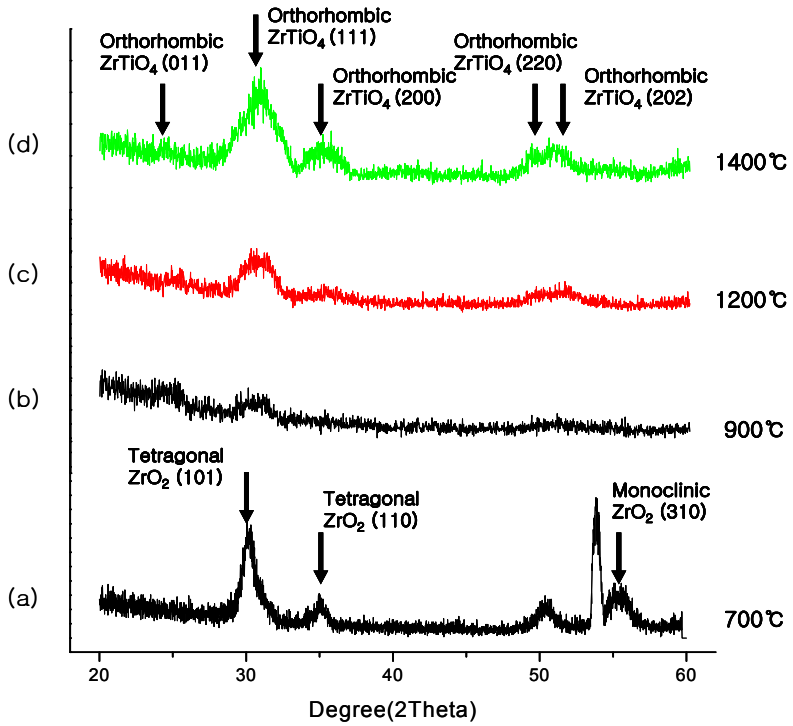

Fig.3. X-ray diffraction patterns of zirconium titanate with a composition of Zr/Ti=65/35 on Si substrates after being annealed at various temperatures under nitrogen for 30 min. The peak at about 54° came from Si(100) substrate.

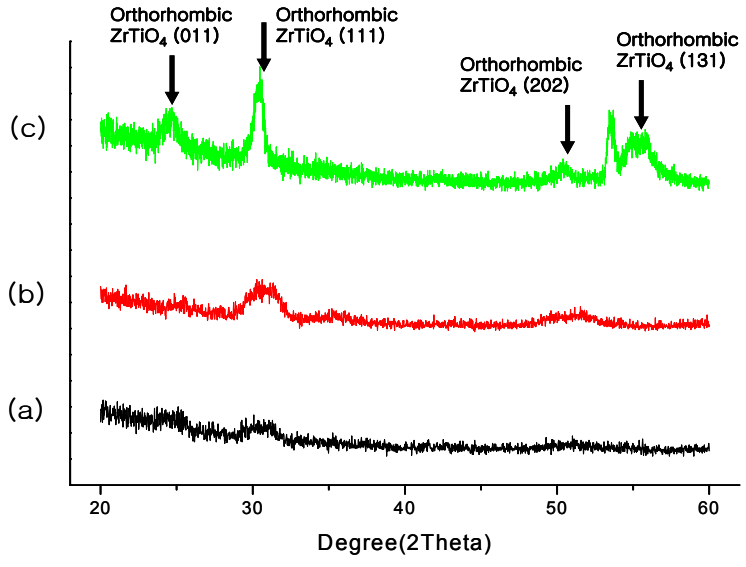

Fig.4. Influence of annealing time on X-ray diffraction patterns of zirconium titanate annealed at 900℃ under nitrogen; (a) 30 min, (b) 60 min and (c) 240 min.

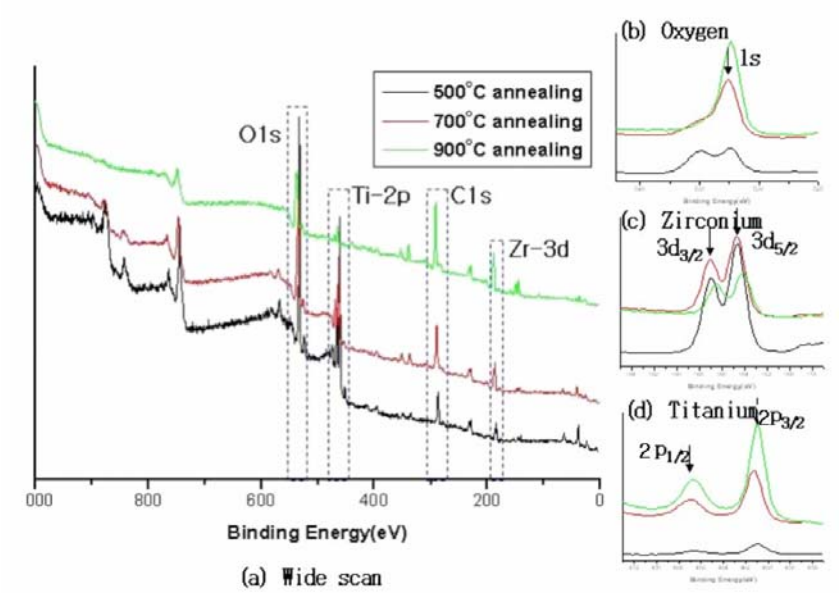

Fig.5. XPS analysis of a multi-layered structure composed of ZrO_2 and TiO_2 thin films after annealing at various temperatures under nitrogen for 30min.