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(出版者 / Publisher)
法政大学イオンビーム工学研究所

(雑誌名 / Journal or Publication Title)
PROCEEDINGS OF THE 33rd SYMPOSIUM ON MATERIALS SCIENCE AND ENGINEERING RESEARCH CENTER OF ION BEAM TECHNOLOGY HOSEI UNIVERSITY (December 10, 2014)

(巻 / Volume)
33

(開始ページ / Start Page)
70

(終了ページ / End Page)
76

(発行年 / Year)
2015-02

(URL)
https://doi.org/10.15002/00031719

CRYSTALLIZATION PROPERTIES OF CeO_2 THIN FILMS DEPOSITED BY MOCVD WITH ADDITIONAL TEOS INTRODUCTION

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Compound thin films consisting of cerium dioxide (CeO_2) and SiO_2 have been deposited on p-type Si (100) substrates by the metal organic chemical vapor deposition (MOCVD) process using tetrakis(3-methyl-3-pentoxy)Cerium($Ce[OC(C_2H_5)_2CH_3]_4$) and tetraethyl orthosilicate (TEOS). The deposition pressure, time, and temperature were 50 Pa, 30 minute, and 350°C, respectively. TEOS was introduced for 5 s or 10 s every 3 min. The post-annealing was performed at 500°C for 30 min in the ambient of air. The X-ray photoelectron spectroscopy (XPS) measurement revealed that the silicate existed in the deposited films with TEOS introduction. The amount of silicon, however, was not changed by the introduction time of TEOS. The X-ray diffraction (XRD) measurement revealed the suppression of crystallization by TEOS introduction; the CeO_2 (111) peak intensity weakened and CeO_2 (200) and CeO_2 (220) peaks disappeared. The TED patterns represented only the amorphous ring in the samples with TEOS introduction.

I. INTRODUCTION

Cerium dioxide (CeO_2) has attracted great interest for gate stack materials of the MOS transistor since CeO_2 has the high dielectric constant of 26 and is compatible with Si in terms of the crystal structure with the small lattice mismatch of 0.35%. However, CeO_2 has a strong tendency to poly-crystallize at relatively low temperatures[1-3)]. Poly-crystallization can lead to increase the leakage current because grain boundaries act as the current path. Amorphous state should be maintained for practical application during the fine structure formation for precise MOS transistor fabrication. We have tried to suppress crystallization by introducing SiO_2, having the different crystal structure, into CeO_2 films by TEOS introduction.

Thermal decomposition temperature of TEOS is above 600°C while deposition rate of CeO_2 thin films significantly decreased more than 400°C[4-5)]. A chemical reaction formula during CeO_2 deposition is $Ce[OC(C_2H_5)_2CH_3]_4 \rightarrow CeO_2 + 4(C_2H_5)_2C{=}CH_2 + 2H_2O$. We have tried to utilize H_2O generated during CeO_2 deposition for hydrolysis

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[#] e-mail: tomonari.furuya.2m@stu.hosei.ac.jp of TEOS.

In this work, we have tried to introduce SiO_2 in CeO_2 films by MOCVD with additional TEOS introduction and compared the crystallization properties in the samples deposited by MOCVD with and without TEOS introduction during the course of post-annealing. We have evaluated crystallinity and composition of the films based on the observation by XTEM, XRD and XPS.

II. EXPERIMENTAL

Cerium dioxide (CeO_2) thin films were fabricated on p-type Si(100) substrates by MOCVD with additional TEOS introduction. The metal-organic sources were tetrakis(3-methyl-3-pentoxy)Cerium$[OC(C_2H_5)_2CH_3]_4$ and tetraethyl orthosilicate (TEOS). After organic removal cleaning, substrates were dipped in a dilute HF solution (4%) for 10 min to remove native oxides. Figure 1 shows the experimental apparatus. The Ce and TEOS source bottle temperatures were maintained at 76°C and room temperature, respectively, to obtain the required vapor pressure of the metalorganic source. Nitrogen was used as the bubbling gas to introduce the source material to the chamber through the thermally stabilized gas line at 110°C. Cerium source gas was supplied through a hole with a diameter of 1 mm for simplifying the deposition gas flow. The distance was 3 cm between the supply point and the substrate. The pressure of the deposition chamber was controlled by the throttle valve connected to the evacuation system and the flow rate of the balance gas introduced from the upper region of the chamber to the deposition region through the distribution plate. The deposition pressure, time, and temperature were 50 Pa, 30 minute, and 350°C, respectively. The flow rates of N_2 carrier gas for Ce and TEOS were 50 sccm and 1 sccm, respectively, and N_2 balance gas 100 sccm. The Ce source was continuously introduced during deposition while TEOS was pulsively introduced for 5 s or 10 s every 3 min. The deposition condition is summarized in Table 1. The post-annealing was performed at 500°C for 30 min in the ambient of air.

Crystallinity of deposited films was examined by XTEM, TED and XRD. Chemical bonding state and composition of deposited films were analyzed by XPS.

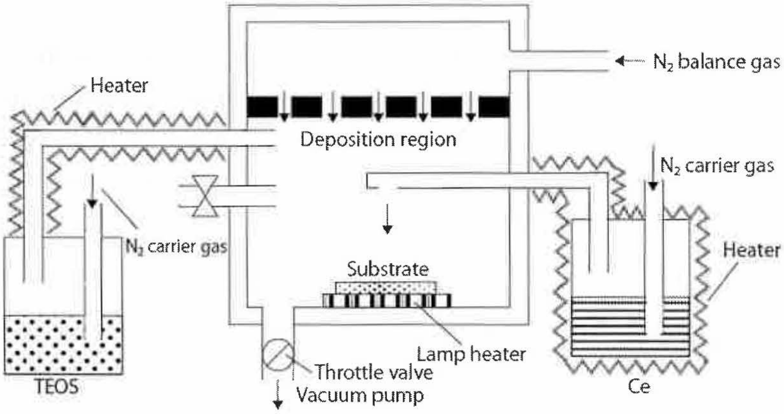


Fig.1 CVD apparatus

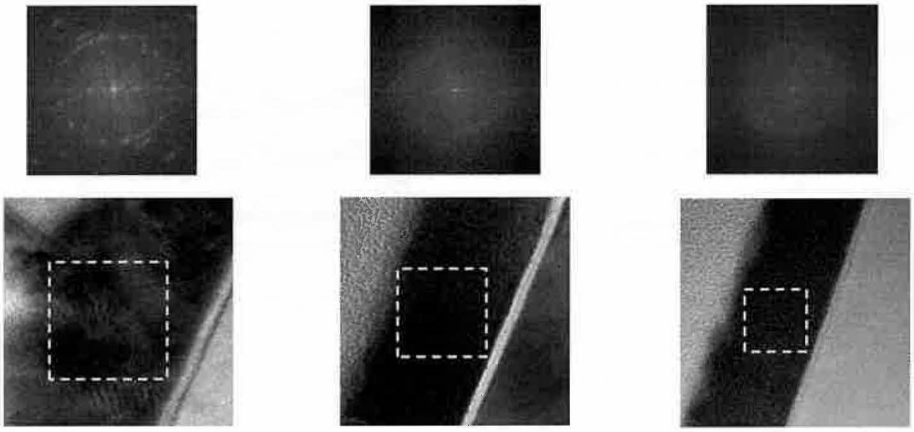
Table1. Deposition condition

Pressure	50 [Pa]
Deposition time	30 [min]
Substrate temperature	350 [°C]
Source bottle temperature (Ce, TEOS)	76 [°C] , R.T.
Balance gas and carrier gas	N_2
Balance gas flow rate	100 [sccm]
Carrier gas flow rate (Ce, TEOS)	50, 1 [sccm]
Ce source introduction	continuous
TEOS introduction	pulsive 5s and 10s every 3 min

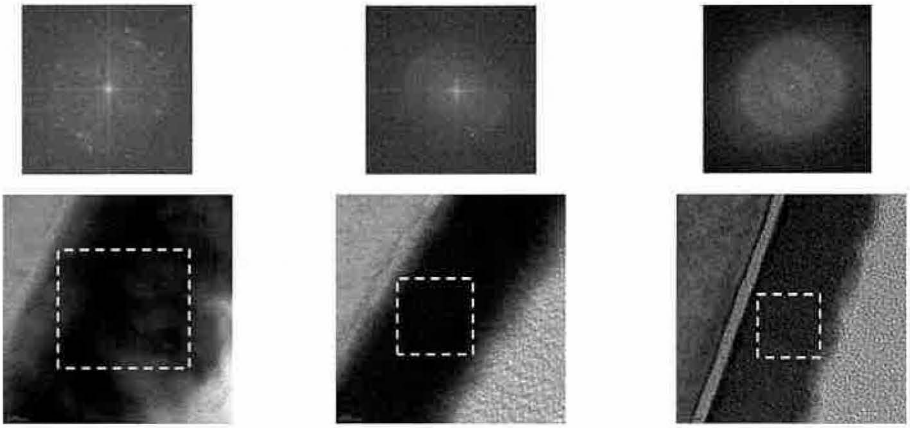
III. RESULTS AND DISCUSSION

Figures 2 (a), (b) and (c) show XTEM images of as-deposited films without and with TEOS introduction for 5 s and 10 s, respectively. Figures 2 (d), (e) and (f) show XTEM images of deposited films without and with TEOS introduction for 5 s and 10 s, respectively, after post-annealing at 500°C for 30 min in the ambient of air. As shown in Figs. 2 (a) and (d) the films were partly crystallized. From Figs. 2 (b), (c), (e) and (f), it is seen that the films were amorphous.

In Fig. 2, TED patterns obtained from the field outlined by broken lines of XTEM images by FFT processing are also shown for the deposited films. As shown in Figs. 2 (a) and (d), the films without TEOS introduction represent the spots on the amorphous ring. Only the amorphous rings appeared in Figs. 2 (b), (c), (e) and (f) for the films with TEOS introduction. From these TED patterns, we concluded that TEOS introduction was effective in suppressing crystallization of the films.



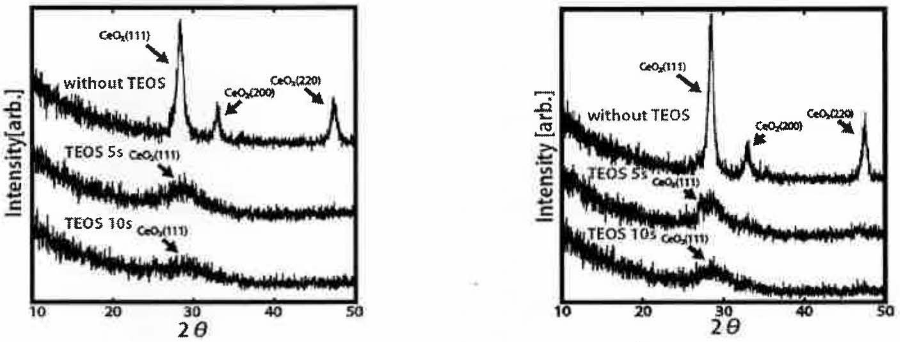
(a) without TEOS (b) TEOS 5 s (c) TEOS 10 s



(d) without TEOS (e) TEOS 5 s (f) TEOS 10 s

Fig. 2 XTEM images of as-deposited films without (a), with TEOS introduction for (b) 5 s and (c) 10 s. XTEM images of the films after post-annealing at 500°C for 30 min in the ambient of air without (d), with TEOS introduction for (e) 5 s and (f) 10 s are also shown. Corresponding TED pattern is shown above the each XTEM images.

Figures 3 (a) and (b) show XRD spectra from as-deposited and post-annealed samples, respectively. By TEOS introduction, CeO_2 (200) and CeO_2 (220) peaks disappeared and the CeO_2 (111) peak intensity weakened, indicating that the CeO_2 films with TEOS introduction were amorphous. These XRD results were consistent with those by XTEM.

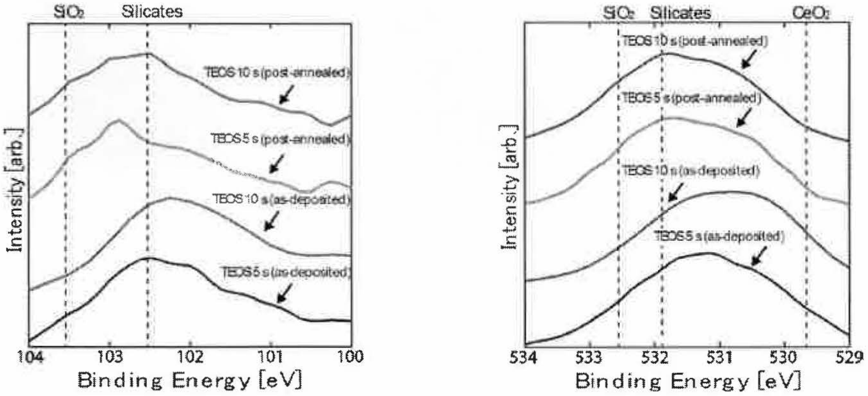


(a) as-deposited

(b) post-annealed

Fig. 3 XRD spectra of deposited films

Figures 4 (a) and (b) show the XPS spectra for Si 2p and O 1s, respectively. Figures 4 (a) and (b) clearly indicate the silicate formation in CeO_2 films by TEOS introduction. From Figs. 4 (a) and (b), Si in the form of SiO_2 was not found in CeO_2 films.

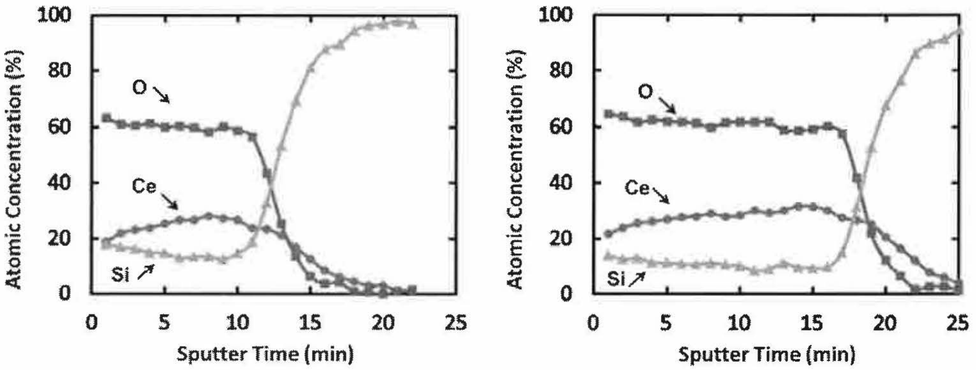


(a) Si 2p spectra

(b) O 1s spectra

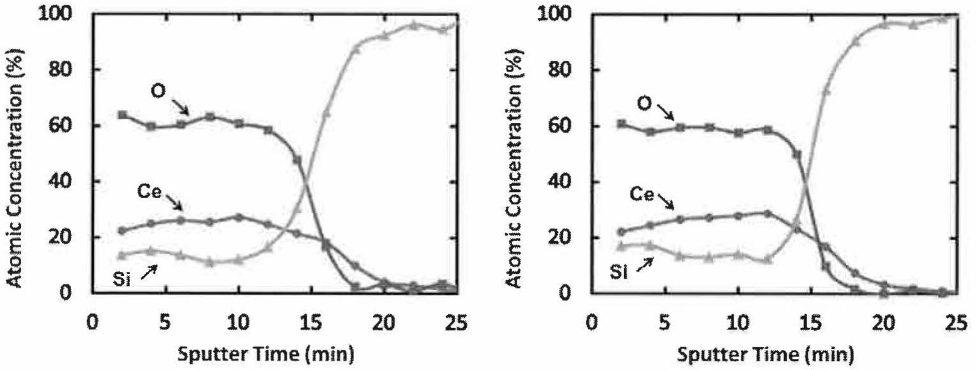
Fig. 4 XPS spectra of CeO_2 films for Si 2p and O 1s. XPS spectra of as-deposited films with TEOS introduction for 5 s and 10 s obtained after sputtering for 5 s. XPS spectra of the films after post-annealing at 500°C for 30 min in the ambient of air with TEOS introduction for 5 s and 10 s obtained after sputtering for 6 s.

Figures 5 (a) and (b) show the XPS depth profiles of as-deposited films with TEOS introduction for 5 s and 10 s. Figures 5 (c) and (d) show XPS depth profiles of the films after post-annealing at 500°C for 30 min in the ambient of air with TEOS introduction for 5 s and 10 s. Figures 5 (a), (b), (c) and (d) indicate that the distribution of Si in CeO_2 films was uniform, despite that TEOS was pulsively introduced. Furthermore TEOS introduction time did not affect the amount of Si in CeO_2 films. These results suggest that the amount of Si in CeO_2 films was limited by H_2O generated during CeO_2 films deposition.



(a) TEOS 5 s - as-deposited.

(b) TEOS 10 s – as-deposited.



(c) TEOS 5 s – post-annealed.

(d) TEOS 10 s – post-annealed.

Fig. 5 XPS depth profiles of as-deposited films with TEOS introduction for (a) 5 s and (b) 10 s and depth profiles of the films after post-annealing at 500°C for 30 min in the ambient of air with TEOS introduction for (c) 5 s and (d) 10 s.

IV. CONCLUSIONS

We succeeded in adding Si in CeO_2 thin films. Si in the form of SiO_2 was not found in CeO_2 films. Silicates were formed in CeO_2 films by TEOS introduction. TEOS introduction time did not affect the amount of Si in CeO_2 films and the distribution of Si in CeO_2 films was uniform. The amount of Si in CeO_2 films was limited by H_2O generated during CeO_2 films deposition. From TED and XRD results, we concluded that crystallization of CeO_2 films was suppressed by forming silicates, having the different crystal structure, in CeO_2 films by TEOS introduction.

ACKNOWLEDGEMENTS

We express our thanks to Dr. Y. Harada, Mr. M. Ichihara and Mr. T. Ueda at the precision analysis Lab., Hosei Universities for their assistance in XPS and XTEM observation.

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