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MOCVD OF CeO_2 AND SiO_2 MIXTURE FILM

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ABSTRACT

Mixture films consisting of Cerium dioxide (CeO_2) and Silicon dioxide ($SiO_{2)}$ were deposited on p-type Si(100) substrates by metal organic chemical vapor deposition (MOCVD), using tetrakis (3-methyl-3-pentoxy) Cerium ($Ce[OC(C_2H_5)_2CH_3]_4$) and tetraethyl orthosilicate (TEOS) for CeO_2 and SiO_2 sources, respectively. Deposition pressure, time and temperature were 50 Pa, 30 min and 350 °C, respectively. While CeO_2 source gas was continuously introduced, TEOS was intermittently introduced for 5 and 10 s every 3 min. Although TEOS was intermittently introduced, Si was uniformly distributed in deposited films. Post-annealing was performed at 500 °C for 30 min in an ambient of air. X-ray photoelectron spectroscopy (XPS) revealed the existence of the silicate in the deposited film. Cross-section transmission electron microscope (XTEM) observation as well as X-ray diffraction (XRD) analysis revealed the suppression of poly-crystallization by introduction of TEOS. Atomic force microscope (AFM) revealed the decrease of surface roughness by the introduction of TEOS.

I. INTRODUCTION

Cerium dioxide (CeO_2) has attracted great interest for gate stack materials of MOS devices because CeO_2 has high dielectric constant of 26, low lattice mismatch of 0.35 % with Si and thermal stability up to 1950 °C. However, CeO_2 has a strong tendency to poly-crystallize at relatively low temperatures$^{1\text{-}3)}$. Poly-crystallization can lead to increase of leakage current along with grain boundaries, and hence amorphous state should be kept to suppress leakage current.

We have planned to suppress poly-crystallization by mixing SiO_2 into CeO_2 films by introducing TEOS during MOCVD. Since deposition temperature of TEOS is higher than 600 °C while deposition rate of CeO_2 significantly decreased more than 400 °C$^{4\text{-}5)}$ in the MOCVD process using $Ce[OC(C_2H_5)_2CH_3]_4$ as a CeO_2 source, it is difficult to perform the simultaneous deposition of Ce and Si oxides by simple pyrolytic MOCVD. The chemical reaction formula during CeO_2 deposition is known as $Ce[OC(C_2H_5)_2CH_3]_4 \rightarrow CeO_2 + 4(C_2H_5)_2C = CH_2 + 2H_2O$. We have tried to utilize

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H_2O generated during CeO_2 deposition for hydrolysis of TEOS, in order to reduce the decomposition of temperature TEOS. Crystallinity and composition of the deposited films were analyzed by XTEM, XRD, XPS and AFM.

II. EXPERIMENTAL

Cerium dioxide (CeO_2) films containing SiO_2 were formed on p-type Si (100) substrates by MOCVD process using metal-organic sources of tetrakis (3-methyl-3-pentoxy) Cerium $[OC(C_2H_5)_2CH_3]_4$ and tetraethyl orthosilicate (TEOS). After organic removal cleaning, Si substrates were dipped in diluted HF solution (4 %) for 10 min to remove SiO_2. Figure 1 shows the MOCVD apparatus. Cerium and TEOS source bottles were kept at 76 °C and room temperature to obtain required vapor pressure of metal organic sources, respectively. Nitrogen was used as the bubbling and carrier gas as well as the balance gas. Cerium source gas was supplied to a substrate through a hole with a diameter of 5 mm. The pressure of deposition chamber was controlled by a throttle valve connected to the evacuation system and the flow rates of balance gas introduced from the upper region of the chamber through the distribution plate. The deposition pressure, time and temperature were 50 Pa, 30 min and 350 °C, respectively. The flow rates of N_2 carrier gas for Ce source, TEOS and the balance gas were 50 sccm, 1 sccm, and 100 sccm, respectively.

The Ce source was continuously introduced during deposition while TEOS was intermittently introduced for 5 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 an 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.

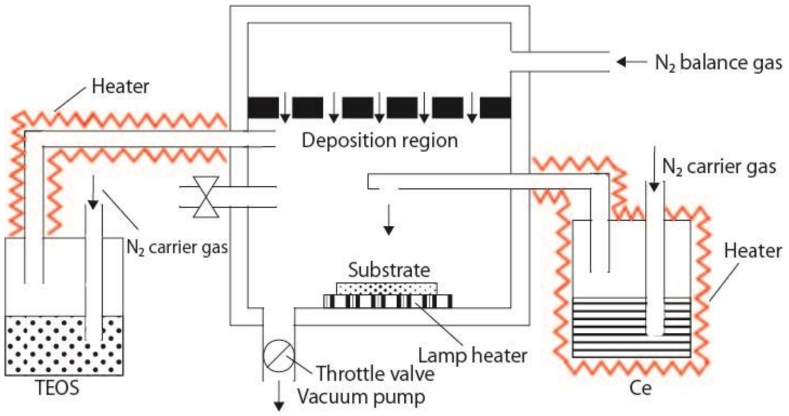


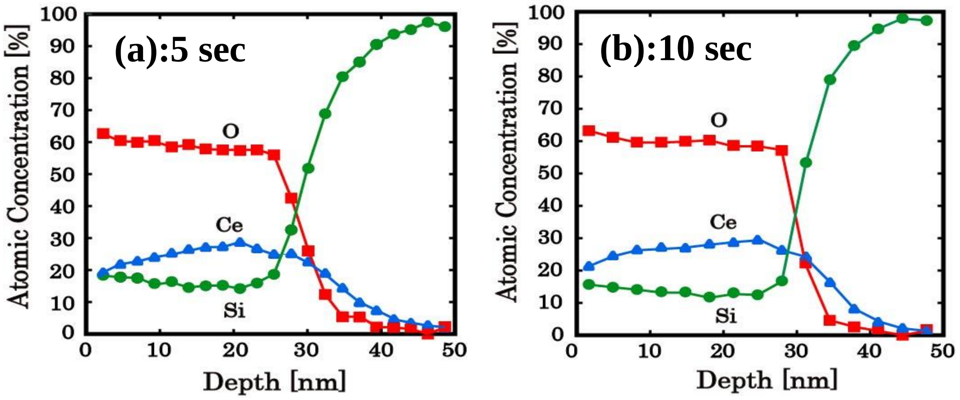
Figure.1 MOCVD apparatus

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	intermittently 5 and 10 s every 3 min

III. RESULTS & DISCUSSION

Figures 2 shows XPS depth profiles of as-deposited films with the introduction period of TEOS for (a) 5 and (b) 10 s. Distribution of Si in the films was uniform in spite of intermittent TEOS introduction. Moreover, the amount of Si in the film was not affected by the period of TEOS introduction. These results suggest that amount of Si in the CeO_2 film was limited by H_2O generated during CeO_2 deposition.

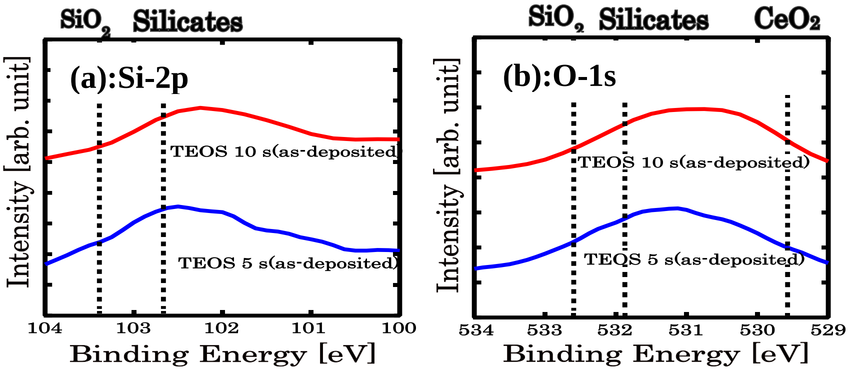


(a): TEOS 5 s

(b): TEOS 10 s

Figures 2. XPS depth profiles of as-deposited films with introduction period of TEOS for (a) 5 and (b) 10 s every 3 min.

Figures 3 (a) and (b) shows XPS Si-2p and O-1s spectra from as-deposited films, respectively. The result indicates that Si exists as a silicate in the deposited films.



Figures 3. XPS Si-2p and O-1s spectra of as-deposited films with introduction of TEOS.

Figures 4 (a) show XTEM images of the as-deposited film without introduction of TEOS, and Figures 4 (b) and (c) show XTEM images of post-annealed films with introduction of TEOS for 5 and 10 s, respectively. Figure 4 (a) indicate poly-crystallization of the film. On the other hand, Figures 4 (b) and (c) indicates that the films were amorphous even after post-annealing. Figures 4 also shows corresponding TED patterns obtained from XTEM images by FFT processing. As shown in Figure 4 (a), diffraction spots representing poly-crystallization exist on the for the film without introduction of TEOS. From these TED patterns, we concluded that TEOS introduction was effective in suppressing crystallization of the films.

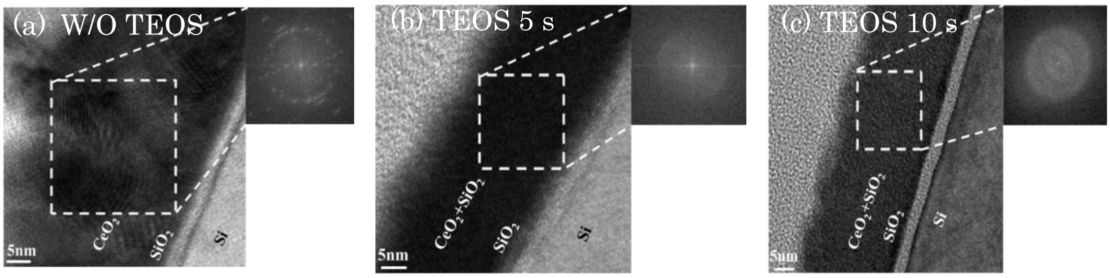
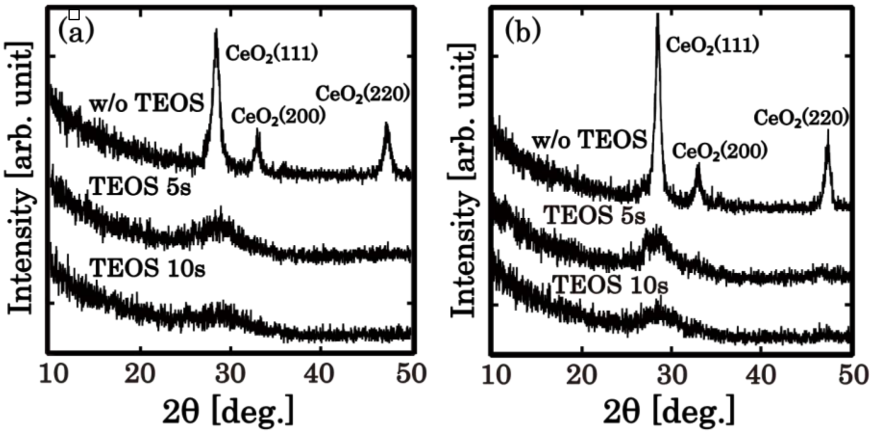


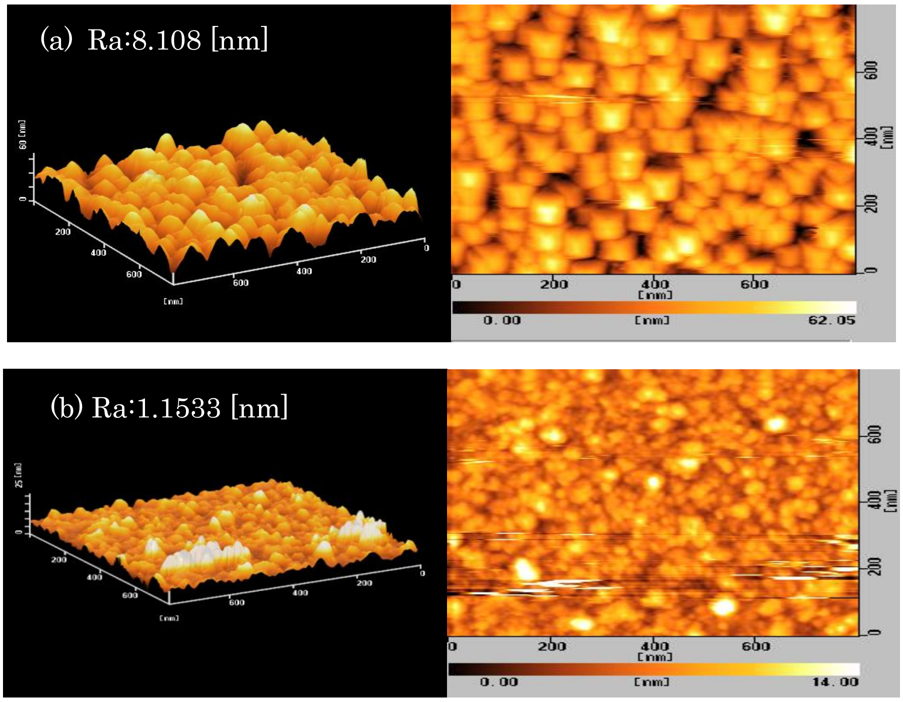
Figure 4 (a). XTEM images of as-deposited films without TEOS, (b) and (c) XTEM images of post-annealed films with introducing TEOS for 5 (b) and 10 s (c), respectively. TED patterns obtained by FFT processing were also shown.

Figures 5 (a) and (b) show XRD patterns of as-deposited and post-annealed films, respectively. It is shown that CeO_2(111) peak intensity weekend and CeO_2(200) and CeO_2(220) peaks disappeared by the introduction of TEOS. The results indicate that the mixture films of CeO_2 and SiO_2 were amorphous. Crystallization of the CeO_2 film was suppressed by introducing TEOS even after 500 ºC annealing.



Figures 5. XRD patterns of (a) as-deposited and (b) post-annealed films

Figures 6 show AFM images of as-deposited films without and with TEOS. The deposited films without TEOS consisted of crystal grains with the average size of 50 nm. By introduction of TEOS, the surface roughness was greatly reduced. On the other hand, the grains size of deposited films with TEOS was much smaller than that of deposited films without TEOS. We consider that the decrease of the surface roughness is attributed to the crystallization suppression by the TEOD introduction as already pointed out by the results of XTEM and XRD.



Figures 6. AFM images of as-deposited films without (a) and with (b) TEOS introduction.

IV. CONCLISIONS

The addition of SiO_2 into CeO_2 films was achieved by the intermittent TEOS introduction during MOCVD of CeO_2 using $[OC(C_2H_5)_2CH_3]_4$. Silicates were formed in the deposited film by TEOS introduction. TEOS introduction period did not affect the amount of Si in the film and the distribution of Si was uniform. The amount of Si in the films was limited by H_2O generated during CeO_2 films deposition. By introduction of TEOS, the surface roughness was greatly reduced.

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