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Fabrication and characteristics of CeO_2 films on Si(1 0 0) substrates by pulsed laser deposition

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Abstract

A detailed investigation about the dependence of film orientation on deposition temperature and ambient oxygen pressure has been carried out for CeO_2 films on Si(1 0 0) substrates using pulsed laser deposition. It has been found that the CeO_2 film orientation varies with increasing oxygen pressure at 750°C deposition temperature. In addition, the recovery of preferential orientation of CeO_2 films grown at 20 Pa ambient oxygen pressure with increasing deposition temperature has also been found for the first time. X-ray photoelectron spectroscopy (XPS) measurements confirm that stoichiometric CeO_2 films can be grown at lower oxygen pressure ($\sim 5 \times 10^{-3}$ Pa). HRTEM result also indicates that the CeO_2 films grown at low oxygen pressure are of high crystallinity. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Epitaxial insulating layer grown on silicon substrates has been attracting great interest due to its potential applicability to silicon-on-insulator (SOI) structures and stable capacitor devices. Cerium dioxide (CeO_2) with cubic fluorite structure (lattice parameter $a_0 = 5.411 \text{ \AA}$) has been con-

sidered one of the most important insulating material because of its desirable properties such as chemical stability and close lattice parameter matching with silicon (lattice parameter $a_0 = 5.430 \text{ \AA}$). The epitaxially growing Si thin films on epitaxial insulating layers deposited on Si single crystal substrates seems to be a better approach for fabricating SOI structure [1–3]. From this view, it is important to grow epitaxial insulating layers on Si substrates.

CeO_2 films have been reported to be epitaxially grown on both (1 0 0)- and (1 1 1)-oriented Si substrates. It was shown that the orientation of CeO_2

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films grown on Si is affected by substrate temperature, ambient oxygen pressure and growth method [1–6]. For example, at a relatively high deposition temperature of 800°C, the orientation of CeO₂ films grown by pulsed laser deposition (PLD) on Si(1 0 0) was found to vary from (1 1 0)-, (1 1 1)- to (1 0 0)-dominant with increasing ambient oxygen pressure. In contrast, (1 1 1)-oriented CeO₂ films can be epitaxially grown on Si(1 1 1) at low oxygen pressure, but contained several percent of (1 0 0) orientation at 15 Pa oxygen pressure.

In this paper, we report that the orientation of CeO₂ films varies on Si(1 0 0) substrates with deposition condition, e.g., ambient oxygen pressure and deposition temperature. The epitaxial layers were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and high-resolution transmission microscopy (HRTEM). The results show that the orientation of CeO₂ films varies with increasing ambient oxygen pressure at 750°C deposition temperature. In addition, the recovery of preferential orientation of CeO₂ films grown at 20 Pa ambient oxygen pressure with increasing deposition temperature has been found for the first time. More specially, (1 0 0)-oriented CeO₂ films can be obtained at low deposition temperature less than 350°C, and then be deteriorated with increasing deposition temperature, finally, it can be recovered at high deposition temperature more than 700°C. XPS results show that stoichiometric CeO₂ films can be grown at ambient oxygen pressure more than 5×10^{-3} Pa. HRTEM result also confirms that CeO₂ film grown at 5×10^{-3} Pa ambient oxygen pressure is high crystallinity.

2. Experimental procedure

The CeO₂ films were prepared on Si(1 0 0) substrates by PLD. The configuration of our laser deposition system has been described previously [7]. Briefly, a XeCl (308 nm) excimer laser beam pulsed at 3 Hz was focused to an energy density of 100 mJ/pulse on stoichiometric CeO₂ ceramic target. The substrate was attached to a resistively heated block opposite the target. Target–substrate spacing was 4 cm. Before deposition, Si(1 0 0) sub-

strates with the size of 10 mm × 4 mm × 1 mm were ultrasonically cleaned in acetone and alcohol, and rinsed in de-ionized water without removal of the native oxide before being put into deposition chamber. The substrate temperature could be raised to appropriate values by a heater on which the substrates were mounted. During all deposition processes, the deposition chamber was prepumped to 8×10^{-4} Pa, and then by introducing O₂ to various oxygen pressure. The deposition rate of CeO₂ films was about 3 Å/s, and the deposition time was 15 min. The crystal structure of the films was investigated by a Rigaku X-ray diffractometer with Cu K_α radiation and a JEOL-2010 HRTEM with point-to-point resolution of 1.94 Å. A VG Escalab5 photoelectron spectrometer with Mg K_α (1253.6 eV) exciting radiation was used to characterize a series of cyclic processes of reduction and reoxidation, and determine the relative amount of surface O- and Ce-species in the CeO₂ films.

3. Results and discussion

Fig. 1 shows the XRD results of the CeO₂ films deposited at a certain temperature 750°C and different oxygen pressure. It was found that the CeO₂ films were (1 1 1) and (L 0 0)-oriented dominant in

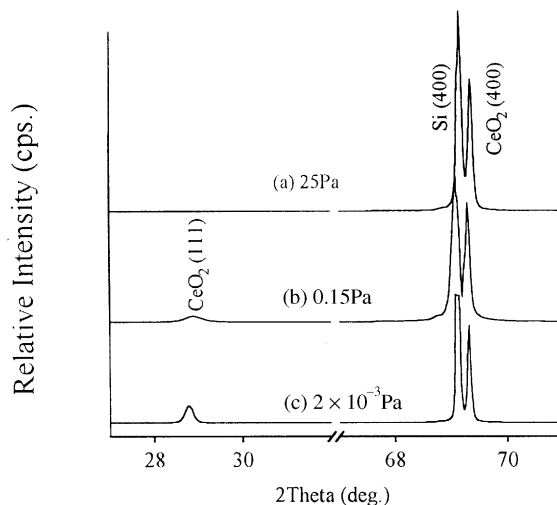


Fig. 1. XRD spectra of CeO₂ films deposited at different ambient oxygen pressure.

our experimental conditions. With increasing oxygen pressure, the XRD intensity of the $\text{CeO}_2(1\ 1\ 1)$ peak decreases and then disappears at 25 Pa oxygen pressure, while the intensity of the $\text{CeO}_2(4\ 0\ 0)$ peak increases. In order to quantitatively confirm the effect of oxygen pressure on the preferential orientation of the CeO_2 films, we define the parameter δ ,

$$\delta = \frac{I_{(4\ 0\ 0)}}{I_{(1\ 1\ 1)} + I_{(4\ 0\ 0)}}, \quad (1)$$

where $I_{(4\ 0\ 0)}$ and $I_{(1\ 1\ 1)}$ are the integral intensity of the $(4\ 0\ 0)$ and $(1\ 1\ 1)$ XRD peaks, respectively. The reason why we choose the $\text{CeO}_2(4\ 0\ 0)$ peak to characterize the orientation of the CeO_2 films but not $(2\ 0\ 0)$ peak could be explained as follows: $(2\ 0\ 0)$ peak in $\text{Si}(1\ 0\ 0)$ substrate is forbidden by extinction condition, but the $(2\ 0\ 0)$ peak will appear if the $\text{Si}(1\ 0\ 0)$ substrate is heated. However, it is difficult to distinguish $\text{Si}(2\ 0\ 0)$ from $\text{CeO}_2(2\ 0\ 0)$ peak due to close lattice match. The difference of the standard 2θ values between Si and $\text{CeO}_2(2\ 0\ 0)$ peaks is about 0.1° , which is just five times bigger than the step (0.02°) in our XRD experiments. By comparison, if we use $\text{CeO}_2(4\ 0\ 0)$ peak as a criterion, the difference of the 2θ values is 0.3° , which is big enough to be distinguished in our experiments.

Fig. 2 presents the ambient oxygen pressure dependence of the preferential orientation parameter δ (squares) and of the relative amount of surface O- to Ce-species. We can see that δ increases with increasing oxygen pressure. Moreover, there a saturation oxygen pressure exists. That is, the CeO_2 films are almost completely $(4\ 0\ 0)$ orientation when oxygen pressure is more than 15 Pa, further increasing oxygen pressure (up to 50 Pa) shows no effect on film preferential orientation.

It was well known that the oxygen pressure plays a significant role on determining the orientation of CeO_2 layers. Early studies showed that, in lower oxygen pressure, the CeO_2 layer could not form perfect crystalline structure probably due to the oxygen deficiency. In higher oxygen pressure, the amorphous SiO_2 layer may be performed on the surface of the substrates, which has also an influence on the crystal orientation of CeO_2 layers [1,3]. In order to identify whether our obtained CeO_2 films

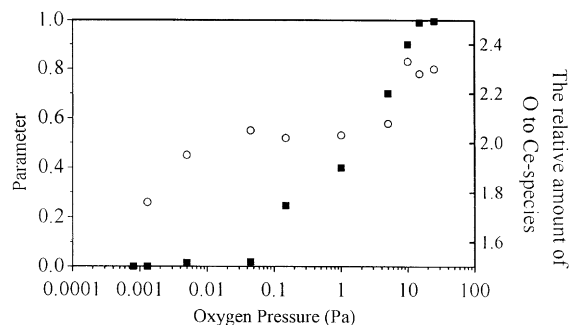


Fig. 2. δ and the relative amount of O- to Ce-species versus ambient oxygen pressure. The squares represent the dependence of δ on ambient oxygen pressure using left axis, while the circles represents the relative amount of O- to Ce-species on ambient oxygen pressure using right axis.

are stoichiometric, we measured by XPS the relative amount of surface O- to Ce-species of the CeO_2 films deposited at different oxygen pressure. Our results for the relative amount of surface O- to Ce-species show that, the CeO_2 films are slight oxygen deficiency in low oxygen pressure less than 10^{-3} Pa, but the amount of oxygen is enough for the CeO_2 films in oxygen pressure more than 5×10^{-3} Pa.

In order to better realize the oxygen atom stability in CeO_2 films, the film deposited at 750°C and 5×10^{-2} Pa oxygen pressure was moved from deposition chamber of PLD system to preparation chamber of Escalab5 photoelectron spectrometer, and then ex situ treated by a series of cyclic processes of reduction and reoxidation, where the temperature varied from room temperature to 600°C , and ambient oxygen pressure from 1×10^{-7} to 1×10^{-3} Pa. The sample was kept at a certain temperature and oxygen pressure for 30 min or 1 h, then cooled to room temperature at the same ambient oxygen pressure. Subsequently, it was transferred to the analysis chamber for XPS studies. Fig. 3a represents Ce 3d spectra of untreated CeO_2 film. Following a detailed assignment of the Ce^{4+} , Ce^{3+} and their mixing structure in Refs. [8,9], Fig. 3a can be attributed to stoichiometric CeO_2 . When this CeO_2 film was treated at 550°C and 2×10^{-5} Pa ambient oxygen pressure for 1 h, a reduction of CeO_2 into Ce_2O_3 can be seen in Fig. 3b. Moreover, Ce_2O_3 can be reoxidized with further treatment at 300°C and 5×10^{-3} Pa ambient oxygen pressure

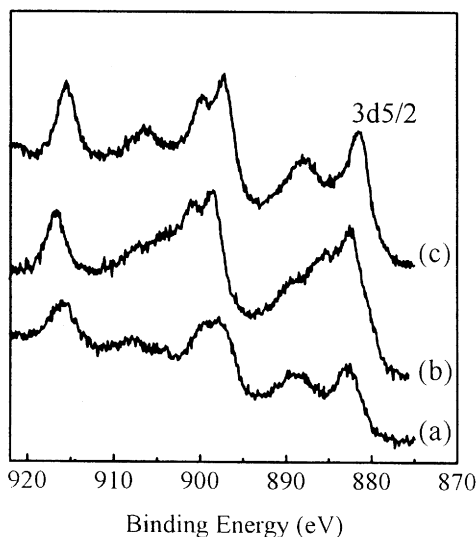


Fig. 3. Ce 3d spectra of CeO_2 films: (a) untreated, (b) treated at 550°C and 2×10^{-5} Pa ambient oxygen pressure for 1 h, (c) treated at 300°C and 5×10^{-3} Pa ambient oxygen pressure for 0.5 h.

for 0.5 h as shown in Fig. 3c. These results suggest that the stoichiometric CeO_2 films can be prepared at ambient oxygen pressure more than 5×10^{-3} Pa, which is in agreement with our obtained relative amount of surface O- and Ce-species.

We have also carried out the experiments of CeO_2 films grown at different deposition temperature in order to understand the influence of deposition temperature on preferential orientation of CeO_2 films. During the processes of these experiments, the ambient oxygen pressure was fixed at 20 Pa and the deposition temperatures were varied from 100 to 850°C . The as-grown CeO_2 films show almost completely (4 0 0) orientation at 100°C , and then a mixing (1 1 1) and (4 0 0) orientation peaks at 550°C . However, completely (4 0 0) orientation peak can be recovered at 700°C . A detailed investigation of the dependence of the preferential orientation parameter δ on deposition temperature was shown in the inset of Fig. 4. It can be seen that, δ varies slowly from 100 to 400°C , but further increasing deposition temperature, δ decreases rapidly and reaches a minimum value at 550°C . If we continue to increase deposition temperature, δ begins to increase and then recovers almost complete (4 0 0) orientation at deposition temperature more

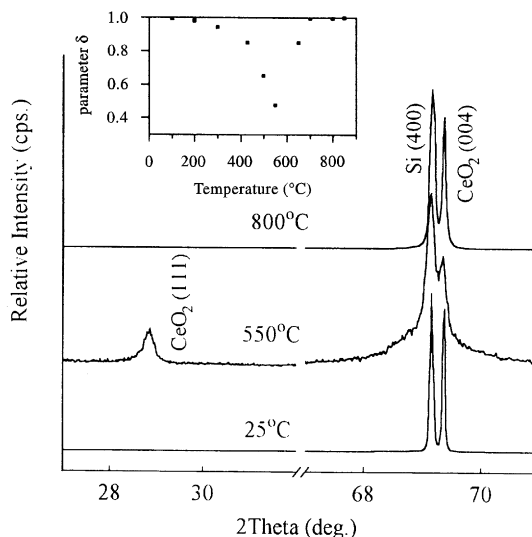


Fig. 4. XRD spectra of CeO_2 films deposited at different temperature. The inset represents the variation of preferential orientation parameter δ with deposition temperature.

than 700°C . The reason about the recovery of the orientation with increasing deposition temperature is still unclear. Kunkel et al. have found a reentrant layer-by-layer growth during molecular beam epitaxy of Pt on Pt(1 1 1), which was ascribed to the change of supercritical nuclei size and the adatom mobility [10]. However, this explanation is not suitable for our results because no experimental proofs shows layer-by-layer growth mode of our CeO_2 films. Nevertheless, it is interesting to compare orientation recovery of $\text{CeO}_2/\text{Si}(1\ 0\ 0)$ with the reentrant layer-by-layer growth of Pt/Pt(1 1 1). Moreover, it will be of beneficial to elucidate the mechanism of $\text{CeO}_2/\text{Si}(1\ 0\ 0)$ growth.

Fig. 5 shows typical HRTEM image including the total contribution of Si, CeO_2 and the interfacial SiO_2 layer of CeO_2 films grown at 5×10^{-3} Pa ambient oxygen pressure and 750°C deposition temperature. From the middle of Fig. 5, we can see an amorphous layer SiO_2 of ~ 50 Å thickness, which was thought to have strong effect on the orientation of CeO_2 films. At the initial stage of the film growth, CeO_2 particles randomly (mainly (1 1 1)-oriented) deposit on the amorphous SiO_2 layer. Then the CeO_2 grains coalesce into a continuous (1 1 1) layer, leaving large undulations at

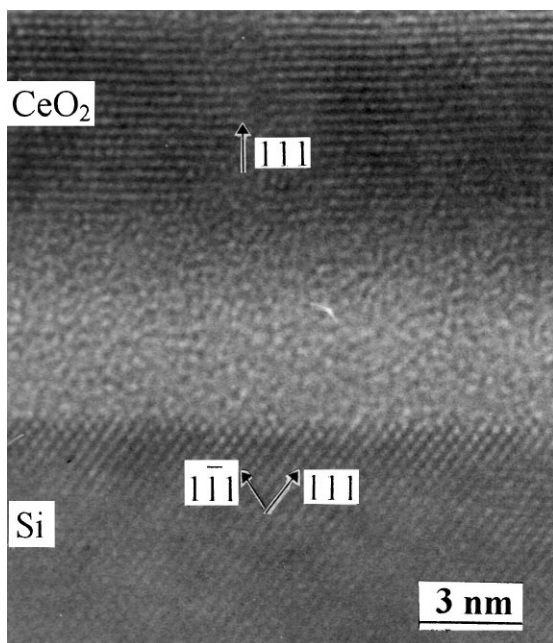


Fig. 5. HRTEM photograph of CeO_2 film deposited at 5×10^{-3} Pa ambient oxygen pressure and 750°C deposition temperature.

the interface between the amorphous and CeO_2 layers. The indices written in Fig. 5 clearly indicate that the Si substrate has a (1 0 0) orientation, and the CeO_2 layer has a (1 1 1) orientation. This orientation relationship obtained from HRTEM is in agreement with that from XRD.

4. Conclusions

In summary, we have carried out a detailed investigation about the orientation of CeO_2 films

grown on Si(1 0 0) substrates under different ambient oxygen pressure and deposition temperature. The experimental results show that the orientation of CeO_2 films varies with increasing ambient oxygen pressure at 750°C deposition temperature. Moreover, the recovery of preferential orientation with increasing deposition temperature has been found in the CeO_2 films grown at 20 Pa ambient oxygen pressure. XPS results show that, the stoichiometric CeO_2 films can be prepared at ambient oxygen pressure more than 5×10^{-3} Pa. HRTEM result also indicates that the CeO_2 films grown at low oxygen pressure are of high crystallinity.

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