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TITLE OF PAPER: Preferred Orientation of Nano-faceted SDC Thin Film Prepared by E-beam Evaporation on Si

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Preferred Orientation of Nano-faceted SDC Thin Film Prepared by E-beam Evaporation on Si

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Abstract The preferred orientation of Sm-doped Ceria (SDC) prepared by E-beam evaporation on Si substrate was investigated. Deposited at room temperature, the amorphous SDC was found, however, the nano triangle-faceted grains were observed when deposited at higher temperature. The preferred orientation of [111] was analyzed when deposited at 100 and 150 °C, however, [220] was found at higher temperature. Moreover, the preferred orientation of SDC changed with thickness was studied. The [111] preferred orientation was formed at lower thickness with higher non-uniformed strain, but [220] was found at higher temperature with lower strain although the (111)
possesses lower surface energy.

**Keywords:** Preferred orientation, E-beam evaporation, Sm-doped Ceria, Strain
1. Introduction

By doping with aliovalent cation (trivalent or divalent), oxygen vacancies are created in the ceria lattice for charge compensation, which may be prepared to give electronic, ionic and mixed modes of conductivity. They are valuable for a variety of applications, such as oxygen-ion conducting electrolytes in solid oxide full cells (SOFCs) operating at intermediate temperature (400-700 °C) [1]. Ceria with a fluorite structure is supposed to be an ideal buffer layer for fabricating epitaxial perovskite materials on silicon substrates because of its excellent lattice match with Si. Preparation of ceria (100) film is more attractive for applications compared to that of (111). Ceria (100) films could be deposited by E-beam assisted evaporation at 750 °C [2], by off-axis RF sputtering at 640-800 °C [3], by metalorganic chemical vapor deposition (MOCVD) at 600-900 °C [4,5], and by combustion chemical vapor deposition at 1000 °C [6]. The excellent epitaxy of ceria films was achieved on a (111) Si substrate without any amorphous layer in the vicinity of the boundary by pulsed laser deposition in an ultrahigh vacuum at room temperature [7]. However, the preferred orientation of ceria on (100) Si substrates reported was not ceria (100) but (110) [8,9]. The epitaxial ceria (110) layers grown on Si(100) substrates at 710 °C had also reported by Inoue et al. [10]. Thus, the preferred orientation of ceria films is determined by prepared method, deposition parameters and substrate. In this study, the
effects of deposition temperature and film thickness were investigated for SDC film prepared by E-beam evaporation method.

2. Experimental Procedure

SDC powder, to be used as the source material for E-beam evaporation, was formed and sintered at 1400 °C for 4 h. The silicon (100) substrate was cleaned in isopropyl alcohol (EPA) and deionized water, and dried by nitrogen gas. A diffusion-pumped vacuum system with a base pressure of $5 \times 10^{-6}$ Torr was used for deposition, and oxygen was introduced into the chamber to adjust the working pressure. For deposition, substrates were fastened in a curved holder with a working distance of 20 cm and heated by irradiation at temperatures of 100, 150, 200 and 250 °C. The deposition rate of SDC was controlled by an E-beam power and monitored by a thickness control system (CRTM-6000, ULVAC, Japan) and various film thicknesses, namely 100, 300, 900 and 1200 nm, were obtained. The structure of SDC films were identified by XRD with Cu Kα radiation and a Ni filter, operated at 30 kV, 30 mA, a scanning rate of 4 °/min and 2 of 20° - 80° (MAX 2500, RIGAKU, Japan). The morphology and cross section of the SDC films were observed by SEM (S4800, HITACHI, Japan).
3. Results and Discussion

The structure of the SDC thin films with thickness of 100 nm prepared by E-beam evaporation has been analyzed by XRD as a function of deposition temperature and shown in Fig.1. Deposited at RT, the structure of the SDC film is amorphous as shown Fig.1 (a), where no reflection peak of the SDC film is found. For thin film deposition, amorphous film is usually obtained when deposited at low temperatures. The mobility of the absorbed species is relatively low, thus preventing these species from migrating to more energetic sites where nucleation can occur [11]. Crystalline ceria film was found when prepared at higher deposition temperature or higher energy bombardment [2]. The crystalline SDC film was prepared at 100 °C and shown in Fig.1 (b), in which the reflections peaks of (111), (200), (220), and (311) of SDC are found meaning that the SDC possessing fluorite structure is obtained although wide full-width at half maximum (FWHM) are found. Figs.1 (c), (d) and (e) show the reflection peaks of the SDC films prepared at 150, 200 and 250 °C, respectively. In these figures, the similar reflection is found although the swing of reflections exists, moreover, the sharp reflections with narrow FWHM are obtained and the high index reflections such as (331) and (420) are observed at high deposition temperature revealing that higher deposition temperature supplied higher mobile energy for absorbed vapor species to improve the crystallization. Fig.1 shows that the crystalline SDC film could be
obtained by E-beam evaporation at temperature as low as 100 °C without any extra energy supplied.

For thin film deposition, texturing growth is commonly found by XRD analysis because of anisotropy surface energy. The lowest surface energy of SDC with fluorite structure is (111), thus, the texturing growth with (111) is in general found as shown in Fig.1. The fluctuation of reflection peaks means some factors were important for SDC deposition. The dependence of the texture coefficients of reflection peaks of SDC on deposition temperature was shown in Fig.2 which according to the TC value calculation [12]. The reflection of (111) possesses the highest TC value, when the SDC film deposited at low temperature which agreed with the report of Sakamoto et al. [1]. At the same time, the reflection peaks of (200) plane possessed the lowest TC values, Sakamoto et al. [1] also pointed out that the (200) preferred orientation was obtained when deposited at high temperature and extra E-beam irradiation was supplied. Therefore, lowest TC(200) value was obtained in this temperature region. However, the TC values of (220) and (311) increased with the deposition temperature. Sakamoto et al. [1] had reported that the (220) preferred orientation is formed at 200 to 400 °C, but the reflection intensities of (220) and (311) are grown and declined. The similar phenomenon has been reported by Cheng et al. [13] to describe the growth characteristics of TiN films prepared by CVD, who pointed out that the interplanar
angle between (220) and (311) is small resulting that the TC(311) increases with the TC(220). Fig. 2 reveals that the (220) may be the preferred orientation of the SDC films prepared at high temperature.

Thin films deposited at high temperature induce internal stress within the film, which might mislead in determining the lattice parameter from one reflection when coatings were under stress. In the measurement of a lattice parameter by way of XRD analysis, a fractional error in $a$ due to the various effects, such as film shrinkage, incorrect radius, off-center specimen, and absorption, are all systematic errors because they vary in a regular way with $\theta$, and decreasing as $\theta$ increases. The systematic errors in $a$ approach zero as $\theta$ approaches 90°, and may be eliminated by use of the proper extrapolation function. Therefore, the Nelson–Riley function in the following equation is utilized to determine the lattice constant [14]. The effect of deposition temperature on lattice constant of SDC films is shown in Fig. 3. The lattice constant of the SDC film between 5.423 and 5.408 Å are obtained when the SDC films prepared at temperature in range from 100 to 250 °C. The lattice constant of SDC film linearly and slightly decreases with deposition temperature in range of 100 and 200 °C, however, the smallest lattice constant is found when SDC film deposited at high temperature, namely 250 °C. According to JCPDs card of No.75-0158, the lattice constant of Sm$_{0.2}$Ce$_{0.8}$O$_{1.9}$ is 5.433 Å. These lattice constants of SDC deposited at various
deposition temperatures are smaller than 5.433 Å.

The diffraction peaks of XRD patterns should be broadened resulted from lattice strain and grain size effect. The relationship between lattice non-uniform strain ($\eta$) and FWHM ($\beta$) can be expressed as Eq.1 [15]:

$$\frac{\beta \cos \theta}{\lambda} = \frac{2\eta \sin \theta}{\lambda} + \frac{1}{d},$$

(1)

where $\theta$ is a Bragg's angle, $\lambda$ is the wavelength of X-ray and $d$ is the crystallite size. For a XRD profile with more than 2 diffraction peaks, the $2\eta$ and $1/d$ could be separately obtained by calculating slope and intercept of profile of $\frac{\sin \theta}{\lambda}$ vs. $\frac{\beta \cos \theta}{\lambda}$.

The lattice strains and grain size are calculated and illustrated in Figs.4 and 5, respectively. Fig.4 shows a maximum non-uniform strain in the films deposited at temperature of 150 °C, however, increasing deposition temperature, the strain in the films decreases and almost no strain is found when deposited at 250 °C. The deposition strain could be partially reduced by the form of amorphous state, however, the strain increases as the crystallization occurred at temperature of 100 °C. Nevertheless, further increase in deposition temperature leads to an increase in mobile energy of vapor species resulting the decrease in films non-uniform strain and increase in crystalline in agreement with the results of XRD and SEM.

The evolution of grain size of the SDC as a function of deposition temperature is calculated from XRD results and shown in Fig.5 which reveals that it decreases with
the increase of deposition temperature and then levels off. This result is in agreement with SEM observation of Fig.7. The deposition temperature is an important parameter for thin films deposition, because the mobile energy of vapor species are supplied by substrate temperature, and the grain size, lattice constant, and strain in the films is apart from the result of Zhang et al. [16] owing to the mobility energy supplyment.

The structure of the SDC films prepared at 150 °C with various thicknesses and the preferred orientation of a film is evaluated by the TC calculation. Fig.6 shows the dependence of TC values on film thickness. For films thickness less than 300 nm, the preferred orientation of SDC is [111], however, the preferred orientation changes to [110] when the film thickness is higher than 300 nm. It reveals that the surface energy dominated in the nucleation and initial growth region. As film thickness increasing, the (220) possesses the highest intensity meaning that the preferred orientation of the SDC films grown in this situation is not [111] but [220]. It is found that the TC values level off with the thickness increasing, which reveals that the preferred orientation is [110] in this deposition condition. The preferred orientation of thin films is considerably determined by prepared method, deposition parameters and substrate. The dependence of preferred orientation of ceria films on deposition temperature had been reported by Sakamoto et al. [2], nevertheless, the effect of thickness on preferred orientation is not discussed simultaneously. Fig.6 reveals that the thickness of 300 nm is a critical
thickness to obtain the preferred orientation of SDC films deposited by E-beam evaporation at 150 °C. According to Fig.4, the highest strain in the SDC films deposited at 150 °C is found. Strain in the films maybe is a key factor for preferred orientation formation.

The morphology of the SDC films with various thicknesses are observed by SEM and shown in Fig.8. In Fig. 7(a) reveals that more nano-pyramidal particles are found on the surface when film thickness is 100 nm, whereas, the triangular grained morphology is found when the film thickness is 1200 nm as shown in Fig.8 (b). When film thickness is low there are a lot of nano-pyramidal grains observed meaning that the nucleation behavior dominated. Nevertheless, there is less nucleation grain found in Fig.7 (b), but large triangular grains are found meaning that the grain growth dominated when the film thickness is high. A morphology of gable-roof-shaped stripes of ceria thin film prepared by E-beam assisted evaporation is found and the preferred orientation of [110] consisting of a pair of (111) facets [17]. From Fig.6, the (111) facetted SDC grains grew with an angle could be deduced.

4. Conclusions

Crystalline SDC film could be prepared at low temperature by E-beam evaporation. Films with high non-uniform strain was found at low deposition temperature resulting
[111] preferred orientation, however, higher deposition temperature resulting nano
triangle-faceted faceted morphology, low non-uniform strain and [220] preferred
orientation. The [111] preferred orientation was also found at lower thickness, namely h
higher non-uniformed strain, but [220] was found at higher temperature with lower
strain although the (111) possesses lower surface energy.

References


Figure Captions

Fig. 1 XRD patterns of the SDC films prepared at (a) RT, (b) 100 °C, (c) 150 °C, (d) 200 °C and (e) 250 °C.

Fig. 2 Texture coefficients of reflections of the SDC films as a function of deposition temperature.

Fig. 3 Dependence of the lattice constant of the SDC films on deposition temperature.

Fig. 4 Dependence of the strain in the SDC films on deposition temperature.

Fig. 5 Dependence of the grain size of the SDC films on the deposition temperature.

Fig. 6 Dependence of texture coefficients of the SDC films on thickness.

Fig. 7 Morphology of the SDC films with thickness of (a) 100 and (b) 1200 nm.
Figure 1
Figure 2
Figure 3

![Graph showing the relationship between lattice constant (Å) and deposition temperature (°C). The graph indicates a decrease in lattice constant as the deposition temperature increases.](image-url)
Figure 4

[Graph showing the relationship between deposition temperature (°C) and strain (%)]
Figure 5

A graph showing the relationship between deposition temperature (°C) and grain size (nm). The graph indicates a decreasing trend in grain size as the deposition temperature increases.
Figure 6

![Graph showing texture coefficients vs. thickness (nm)]
Figure 7