

## CRYSTALLINE STRUCTURE OF YSZ THIN FILMS DEPOSITED ON Si(111) SUBSTRATE BY CHEMICAL VAPOR DEPOSITION

Sang-Chul Hwang, Hee-Gyoun Lee\* and Hyung-Shik Shin<sup>†</sup>

School of Chemical Engineering, Chonbuk National University, Chonju, Chonbuk 561-756, Korea

\*Superconductivity Research Department, Korea Atomic Energy Research Institute,  
P.O.Box 105, Taejeon 305-600, Korea

(Received 1 February 1997 • accepted 28 February 1998)

**Abstract** – Yttria-stabilized zirconia (YSZ) thin films were formed on Si(111) substrate by chemical vapor deposition (CVD) in a temperature range of 650-800 °C using  $\beta$ -diketone metal chelates. The scanning electron microscopy (SEM) and X-ray diffraction (XRD) data evidenced that YSZ thin films have a smooth surface with fine grains and crystalline structure, respectively. The crystalline structure of YSZ films was affected by the deposition temperature. The X-ray photoelectron spectroscopy (XPS) data indicated that the YSZ film grows thick enough to prevent the diffusion of Si.

Key words: YSZ Thin Film, Si Substrate, CVD, XPS, XRD

### INTRODUCTION

Thin films of yttria-stabilized zirconia (YSZ) are considered to be useful for various applications such as optical coating, solid electrolytes in a solid oxide fuel cell, high-temperature water vapor electrolysis HTE-cells and thermal barrier layers. YSZ thin films have recently also attracted much attention in the preparation of  $Y_1Ba_2Cu_3O_{7-x}$  (YBCO) high- $T_c$  superconducting thin films on Si substrate as a buffer layer, on the basis of the fact that YSZ films on Si substrate have no reaction and the lattice matches to Si [Hashimoto et al., 1988] within 6 % as can be seen in Table 1. If a direct deposition of high- $T_c$  superconducting materials on popular semiconductor substrate such as Si can be made, it would accelerate its applicability in microelectronics. However, it has not been successful, mainly due to a high diffusion or chemical reaction between Si substrate and the superconductor [Komatsu et al., 1988]. To overcome those difficulties, low temperature deposition or introduction of a buffer layer has been carried out. The most important point in microelectronic application is the control of YSZ grain orientation because the quality of the subsequently deposited YBCO thin films depends on the crystallographic orientation of YSZ buffer layers. From the viewpoint of texturization, buffer layers are necessary to produce uniaxially (c-axis) or biaxially (in-plane aligned) to assist the texturization of superconducting thin films. It has been reported that the YSZ thin films can be obtained by several deposition techniques, such as off-normal ion beam assisted deposition (IBAD) [Iijima et al., 1992], ion assisted laser ablation [Reade et al., 1992] and magnetron sputtering [Chatterjee et al., 1994].

In the present paper, we report the preparation of thin

Table 1. Relevant parameters of YBCO and some substrate materials

Material	Structure	Lattice constant (Å)	Thermal expansion coefficient ( $10^{-6}/^{\circ}\text{C}$ )
Si	diamond	5.43	3.8
SiO <sub>2</sub>	hexagonal	a=4.90 b=5.39	3.2
YSZ	cubic	5.15	11
YBCO	orthorhombic	a=3.83 b=3.89 c=11.7	8.5

films of YSZ on Si(111) substrates by the CVD method, focusing on the effects of preparation conditions on the thickness, morphology, and crystalline structure of the films.

### EXPERIMENTAL

YSZ film deposition was carried out in a hot-wall type CVD reactor, described in detail elsewhere [Shin et al., 1993]. Source materials used were  $\beta$ -diketone chelates of Y(thd)<sub>3</sub> and Zr(thd)<sub>4</sub> (thd=2,2,6,6-tetramethyl-3,5-heptanedionate) (Strem Co., Ltd., USA). These chelates were evaporated at 122 °C and 180 °C, respectively. The source vapors of Y and Zr were transported into the hot zone by Ar gas independently and oxygen gas was introduced separately. Deposition of films was performed on a p-type Si(111) substrate placed normal to a gas stream at a substrate temperature of 600-800 °C. The Si wafers were cleaned in dilute HF solutions to remove the native oxide layer from the surface before each experiment. During deposition, oxygen partial pressure was maintained at 0.27 torr. The crystalline properties and components of deposited layers were investigated by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS), respectively. Surface

<sup>†</sup>To whom all correspondence should be addressed.  
E-mail : hsshin@che.chonbuk.ac.kr

morphology was observed by using scanning electron microscopy (SEM). Average film thickness was measured by an  $\alpha$ -step profilometer.

## RESULTS AND DISCUSSION

The deposition condition for YSZ thin films is shown in Table 2. Fig. 1 illustrates the X-ray diffraction patterns of the YSZ films deposited on Si(111) substrates in terms of deposition temperature. The crystal phases depend strongly on deposition temperature. The film showed no crystalline orientation below 650°C, indicating that a higher temperature is required for the deposition of the film. All the films formed in a temperature range from 700 to 800°C were composed of only YSZ phases. As shown in the figure, the films formed at 750°C had c-axis orientation and above 800°C had preferred orientation showing stronger XRD peaks of (111) than the other peaks.

A scanning electron micrograph of the surface of YSZ thin film prepared at 750°C for 30 min is shown in Fig. 2. The

adhesion of the film on the surface was quite strong. The average grain sizes were estimated to be 0.2  $\mu\text{m}$  and these films were dense and had a mirrorlike surface.

Fig. 3 shows an X-ray photoelectron survey spectrum after 30 minutes of  $\text{Ar}^+$  ion sputtering. YSZ films of about 450 nm thick on the average were deposited on Si(111) substrate at 750°C. As seen in the figure, Zr peaks (183, 332, 346 and 431 eV) and Y peaks (158 and 299 eV) were pronounced, but Si peaks were not detected, which means that Si was not diffused through the YSZ films.

Table 3 lists the deposition rate of YSZ films according to the substrate temperature under the deposition condition described in Table 2. The deposition rate increased with the substrate temperature.

Fig. 4 shows the variation of the film thickness with deposition time at 750°C. The average deposition rate was 20 nm/min. An Arrhenius plot for the YSZ thin film deposition is given in Fig. 5. The Arrhenius plot was not linear. A change in activation energy with temperature indicates a shift in the controlling mechanism of the reaction. The temperature de-

Table 2. Deposition condition for YSZ film

Source material	Source temp.(°C)	Carrier gas flow rate (ml/min)	Substrate temp.(°C)
Y(thd) <sub>3</sub>	122	280	600-800
Zr(thd) <sub>4</sub>	180	280	

Total gas flow rate : 600 ml/min

O<sub>2</sub> partial pressure : 0.27 torr

Ar partial pressure : 0.73 torr

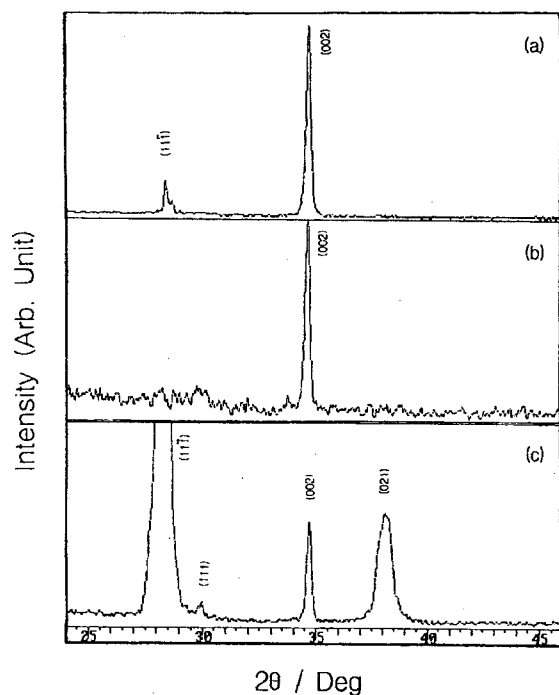


Fig. 1. XRD patterns of the YSZ films prepared on Si(111) substrate as a function of temperature.

(a) 700, (b) 750, and (c) 800°C.

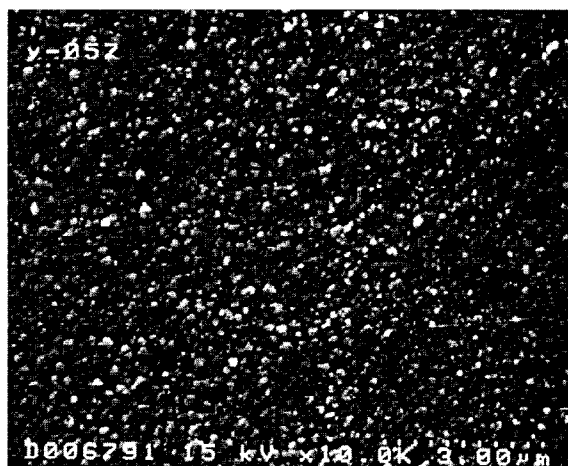


Fig. 2. SEM micrograph of a typical YSZ film on Si(111) at 750°C.

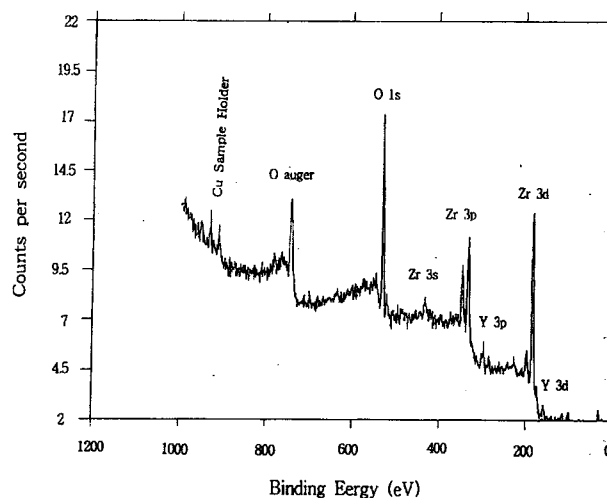
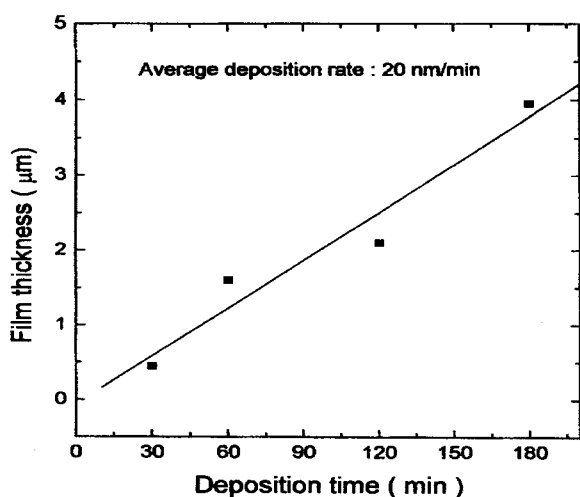
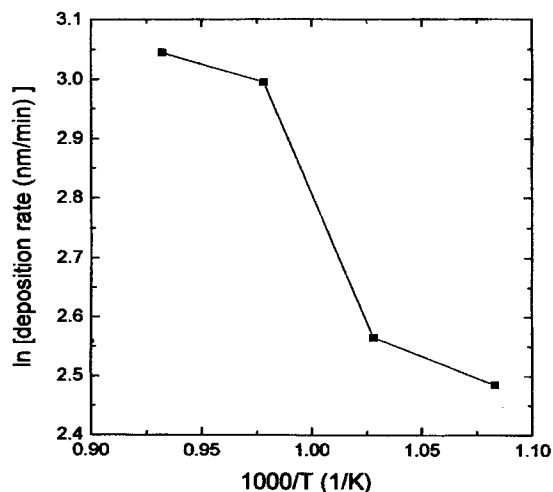


Fig. 3. X-ray photoelectron spectrum of YSZ film deposited on Si(111) at 750°C.

**Table 3. Deposition rate of YSZ thin films vs. substrate temperature under the deposition condition listed in Table 2**

Substrate temperature (°C)	Deposition rate (nm/min)
650	12
700	13
750	20
800	21

**Fig. 4. Plot of film thickness vs. deposition time for YSZ film at 750°C.****Fig. 5. Arrhenius plot for the deposition of YSZ thin film.**

pendence of the deposition rate of YSZ on Si substrate deposited by CVD from the decomposition of  $\beta$ -diketone metal chelates exhibits three temperature intervals. In the first interval, up to about 700°C, the temperature insensitivity of growth rate may be attributed to interdiffusion of reactants. In the second interval, between 700 and 750°C, the reaction

rate increased with temperature. This means that in that region the reaction rate is limited by kinetics at or near the substrate. This is the regime desired in hot-wall type CVD reactors. Above 750°C, the growth rate decreased because of an increased desorption rate and depletion of reactants on reactor walls.

## CONCLUSION

YSZ thin films could be grown on the Si(111) substrate by CVD in a temperature range from 650 to 800°C, with a focus on the effects of preparation conditions on the deposition rate, morphology, and crystalline structure of the films. The deposited films were dense and had a mirrorlike surface. The crystalline structure of YSZ films was affected by the deposition temperature, while the (002) plane of the film was dominant at 750°C. The effect of temperature on the growth rate of YSZ layers was discussed. Up to about 700°C, film growth is diffusion-controlled. Above 700°C, the growth kinetics are controlled by the surface reaction.

## ACKNOWLEDGEMENTS

The authors are grateful for the financial support from Korea Science and Engineering Foundation under Research Contract No. 951-1105-015-2.

## REFERENCES

- Chatterjee, R., Fukutomi, M., Aoki, S., Togano, K. and Maeda, H., "Study of  $Y_1Ba_2Cu_3O_{7-\delta}$  Film Growth on (200) Oriented Yttria Stabilized Zirconia Buffer Layer on Metallic Substrates", *Appl. Phys. Lett.*, **65**, 109 (1994).
- Hashimoto, T., Fueki, K., Kishi, A., Azumi, T. and Koinuma, H., "Thermal Expansion Coefficients of High- $T_c$  Superconductors", *Jpn. J. Appl. Phys.*, **27**, L214 (1988).
- Iijima, Y., Tanabe, N., Kohno, O. and Ikeno, Y., "In-plane Aligned  $YBa_2Cu_3O_{7-x}$  Thin Films Deposited on Polycrystalline Metallic Substrates", *Appl. Phys. Lett.*, **60**, 769 (1992).
- Komatsu, T., Tanaka, O., Matusita, K., Takata, M. and Yamashita, T., "On the Reaction of Quenched  $BaYCuO$  Powders with Various Materials", *Jpn. J. Appl. Phys.*, **27**, L 1025 (1988).
- Reade, R. P., Berdahl, P., Russo, R. E. and Garrison, S. M., "Laser Deposition of Biaxially Textured Yttria-stabilized Zirconia Buffer Layers on Polycrystalline Metallic Alloys for High Critical Current Y-Ba-Cu-O Thin Films", *Appl. Phys. Lett.*, **61**, 2231 (1992).
- Shin, H. S., Cho, I. J., Park, J. S., Yang, S. W., Lee, H. G. and Won, D. Y., "A Study on the Property Changes According to Surface States of Substrate in the Preparation of Y-Ba-Cu-O High- $T_c$  Superconducting Thin Films by Chemical Vapor Deposition", *HWAHAK KONGHAK*, **31**, 131 (1993).