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# Proposal of general rule to prepare epitaxial ceramic thin films at low temperature from the point of crystal chemistry

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**Abstract**

We have succeeded to prepare epitaxial yttria stabilized zirconia (YSZ) thin films at room temperature (27 °C) by the use of nm thick YSZ buffer layer deposited at 800 °C on Si(0 0 1) substrate. Room temperature epitaxial growth was realized on 0.8 nm thick ultra thin YSZ buffer layer, however, to achieve high crystallinity, 6.7 nm thick was needed. On the 6.7 nm thick YSZ buffered Si(0 0 1) substrate, we have tried to prepare epitaxial oxide ceramic thin films. As the result, epitaxial $CeO_2$, $In_2O_3$, and MnZn-ferrite thin films were successfully deposited even at room temperature. The conditions of epitaxial growth at such low temperature was considered from the point of crystal chemistry. As the result, following conditions were proposed:

(1) Materials with both small lattice mismatch and small electronegativity difference; or
(2) Materials with small lattice mismatch and composed of single component.

These proposed conditions will helpful to design epitaxial growth of oxide ceramic thin film at low temperature.


*Keywords:* A. Film; Low temperature; Epitaxial; Buffer layer; Electronegativity

## 1. Introduction

Preparation of heteroepitaxial ceramic thin films at room temperature is very attractive from the point of both scientific and engineering aspects because interdiffusion between oxide films and substrates would be significantly suppressed to obtain sharp interface. Therefore, it is expected that the room temperature epitaxial process would improve the properties of foregone oxide thin film devices such as ferroelectric random access memory (FeRAM) and high-*k* dielectrics. The room temperature deposition processes also have a potential to create novel oxide/semiconductor monolithic devices. In addition, by using this room temperature deposition, it would be possible to use low heat resistance materials such as polymers as the substrates of film deposition.

We have reported preparation of epitaxial yttria stabilized zirconia (YSZ) at room temperature (27 °C) on YSZ buffered Si(0 0 1) substrate (two-step deposition) [1]. In our previous work, we found that ultra thin (>0.8 nm thick) YSZ buffer layer deposited at high temperature (800 °C) helped the preparation of epitaxial growth of YSZ at room temperature. In the previous work, the thickness of YSZ buffer layer was fixed to 0.8 nm. Therefore, the effect of thickness of initial YSZ buffer layer on the crystallinity of YSZ thin film deposited at room temperature was not clarified yet.

In the literature, epitaxial growth of oxide ceramic thin films at room temperature has been reported for several materials. The reported results were briefly summarized in Table 1 from the points of material, substrate, deposition temperature and deposition method. In these literatures, the description concerning the epitaxial growth phenomena at room temperature for individual materials, however, the general consideration for the conditions or guidelines why it was possible to realize epitaxial growth even at such low temperature.

We have two purposes in this work. One is to clarify the effect of nanometer thick YSZ buffer layers for the epitaxial growth of YSZ and many other materials at room

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Table 1
List of epitaxial growth at around room temperature in the literature

| Film material | Substrate | Deposition temperature (°C) | Deposition method | References |
|---|---|---|---|---|
| YSZ | YSZ/Si(0 0 1) | 27 | PLD | [1] |
| MgO | MgO(0 0 1) | −133 | MBE | [2] |
| $CeO_2$ | Si(1 1 1) | 20 | PLD | [3] |
| $CeO_2$ | YSZ/Si(0 0 1) | 20 | PLD | [4,5] |
| BaO | $SrTiO_3$(0 0 1) | 20 | PLD | [6] |
| NiZn- and MnZn-ferrite | $Al_2O_3$(0 0 0 1) | Room temperature | PLD | [7,8] |
| ITO | $CeO_2$/Si(1 1 1) | 20 | PLD | [9] |

MBE: molecular beam epitaxy; PLD: pulsed laser deposition; YSZ: yttria-stabilized zirconia; ITO: indium tin oxide.

temperature. Another purpose is to propose conditions of epitaxial growth at room temperature from the point of crystal chemistry.

## 2. Experimental

All films were deposited by pulsed laser deposition (PLD) method with KrF excimer laser ($l = 248$ nm) using ceramic targets. The laser beam (7 Hz) was focused by a fused silica lens up to an energy density of around 2.0 J/cm$^2$ and an angle of 45° on rotating targets. Two-step deposition process was used to examine epitaxial growth of various oxide ceramic thin films. As the first step, nm thick very thin YSZ buffer layer was deposited at 800 °C under $8.0 \times 10^{-5}$ Pa $O_2$ on Si(0 0 1) substrate with native $SiO_2$ layer. The thickness of native $SiO_2$ measured by X-ray photoelectron spectroscopy (XPS) was 1.1 nm. The deposition rate of YSZ was 6.3 nm/min and the thickness of YSZ buffer layer was controlled between 0.4 and 6.7 nm by changing deposition period. After deposition of YSZ buffer layer at 800 °C, the substrate was cooled down to room temperature (27 °C). then second step was proceeded. At room temperature, various kind of oxide was deposited on the YSZ buffered Si(0 0 1) substrates under $8.0 \times 10^{-5}$ Pa $O_2$. Oxide materials tried to deposit at room temperature were YSZ and $CeO_2$ with fluorite structure, $In_2O_3$ and $Y_2O_3$ with c-rare earth structure, MnZn-ferrite ($Mn_{0.22}Zn_{0.08}Fe_{0.70}O_4$) with spinel structure, $TiO_2$ with rutile structure, $Y_2Ti_2O_7$ with pyrochlore, $Pb(Zr_{0.5}Ti_{0.5})O_3$, $SrTiO_3$, and $BaTiO_3$ with perovskite structure. The growth behavior was in-situ monitored by reflection high speed electron diffraction (RHEED) operated at 25 kV. The composition and thickness of the films were determined by wavelength dispersive X-ray fluorescent spectroscopy (XRF). The thickness of the oxide films deposited at room temperature was between 50 and 150 nm.

## 3. Results and discussions

### 3.1. Effect of thickness of 800 °C deposited YSZ buffer layer on the crystallinity of room temperature-deposited YSZ thin films

Fig. 1 shows the change of X-ray diffraction (XRD) patterns of 27 °C deposited 64 nm thick YSZ thin films with the thickness of 800 °C deposited YSZ buffer layers. The thicknesses of 800 °C deposited YSZ buffer layers were: (a) 0.4, (b) 0.8, (c) 1.7, (d) 3.4, and (e) 6.7 nm. This figure indicates that 27 °C deposited YSZ thin film was amorphous when the thickness of 800 °C deposited YSZ buffer layer was 0.4 nm, and crystallization occurs when the thickness of 800 °C deposited YSZ buffer layer was more than 0.8 nm. The peak intensity of 27 °C deposited YSZ(0 0 2) thin film was increased with the thickness of 800 °C deposited YSZ buffer layer. In plane orientation of 27 °C deposited YSZ(0 0 2) thin film was examined with in-situ RHEED observations. Fig. 2a shows an RHEED image of 800 °C deposited YSZ buffer layer. Since the thickness of YSZ buffer layer was very thin (0.8 nm), obvious streak was not observed. However, 27 °C deposited YSZ thin film deposited on the 0.8 nm thick YSZ buffer layer shows streak pattern (Fig. 2b). Obvious streak pattern was observed when the thickness of 800 °C deposited YSZ was 6.7 nm (Fig. 2c). 27 °C deposited YSZ thin film deposited on the buffer layer showed sharp streak pattern (Fig. 2d). The fact that same RHEED patterns were observed in Fig. 2b–d shows that all 27 °C deposited YSZ thin films were epitaxially grown on Si(0 0 1) substrates with cube-on-cube relation. To evaluate the degree of crystallinity of YSZ thin films, the change of full-width half-maximum (FWHM) of omega scanning (rocking curve) with the thickness of 800 °C deposited YSZ buffer layers was measured for YSZ(0 0 2) diffraction peak (Fig. 3). This figure indicates that the degree of FWHM was decreased with the thickness

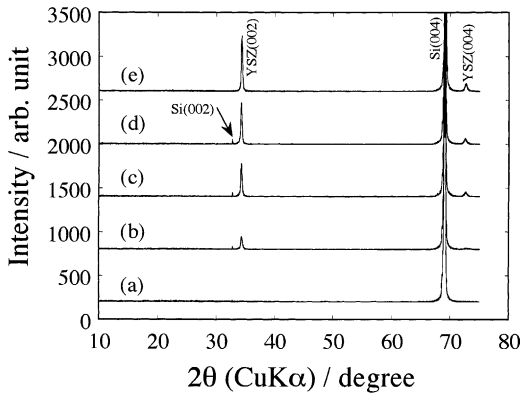


Fig. 1. Change of XRD patterns of 27 °C deposited YSZ thin films with the thickness of 800 °C deposited YSZ buffer layers. The thickness of buffer layers were: (a) 0.4, (b) 0.8, (c) 1.7, (d) 3.4, and (e) 6.7 nm.

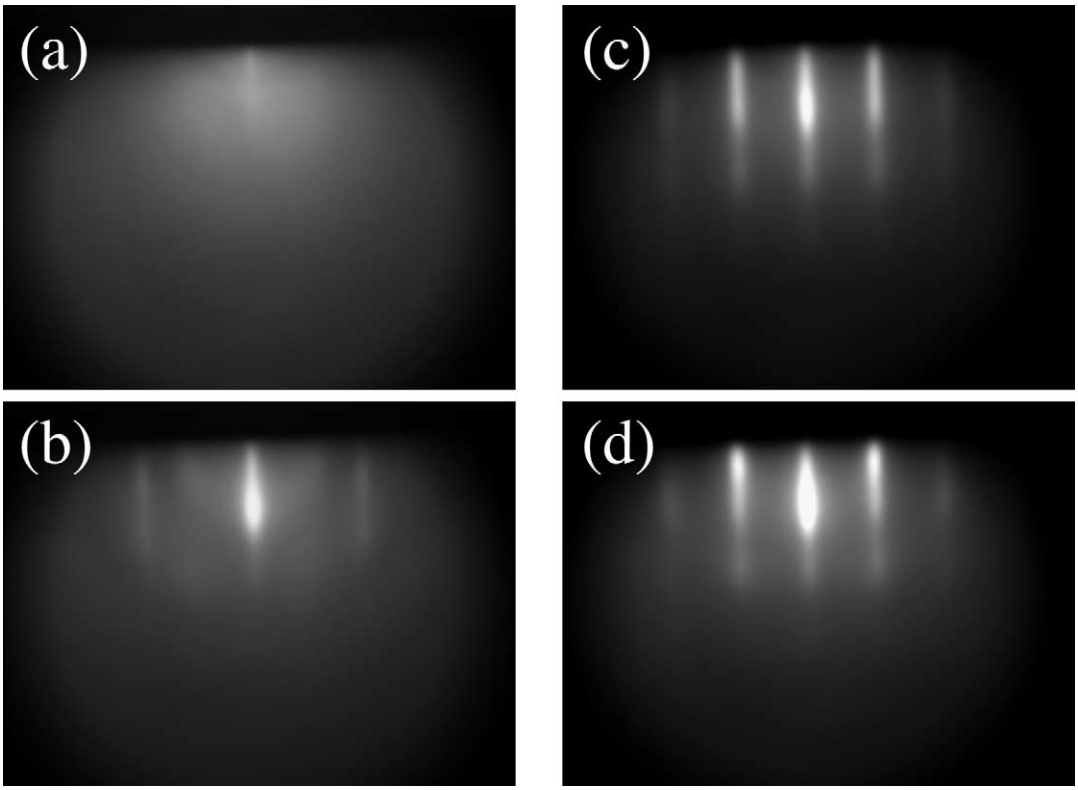


Fig. 2. RHEED images of: (a) YSZ buffer layer (800 °C, 0.8 nm), (b) YSZ thin film deposited on (a) (27 °C, 64 nm), (c) YSZ buffer layer (800 °C, 6.7 nm), (d) YSZ thin film deposited on (c) (27 °C, 64 nm).

of 800 °C deposited YSZ buffer layer, however, the difference of FWHM value of YSZ thin film deposited on 3.4 and 6.7 nm thick YSZ buffer layer was small. This means that 6.7 nm is enough thickness for YSZ buffer layer to help crystallization even at 27 °C. Therefore, in the following experiments, the thickness of 800 °C deposited YSZ buffer layer was fixed to 6.7 nm. It should be noted that epitaxial YSZ thin film was actually prepared at even 27 °C, the lattice parameter of 27 °C deposited YSZ was different from that of 800 °C deposited one. Fig. 4 shows the change of lattice parameter of YSZ thin films deposited on 800 °C deposited YSZ buffer layers with deposition temperature. This figure indicates that the lattice parameter of YSZ thin films deposited at 27, 200, and 400 °C was apparently larger than that deposited at 600 and 800 °C. To examine the stability of lattice parameter, the YSZ film deposited at 27 °C was annealed at 400 °C for 2 h in $1.01 \times 10^5$ Pa $O_2$. After annealing, the lattice parameter of 27 °C deposited YSZ thin film was decreased and approached to those of 600 and 800 °C deposited ones. This suggests that 27 °C deposited YSZ thin film contains some kind of defects such as oxygen vacancy compare to 800 °C deposited ones.

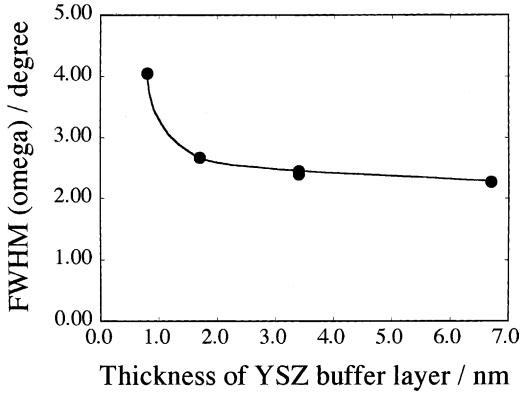


Fig. 3. Change of FWHM (omega) of 27 °C deposited YSZ thin films with the thickness of 800 °C deposited YSZ buffer layers.

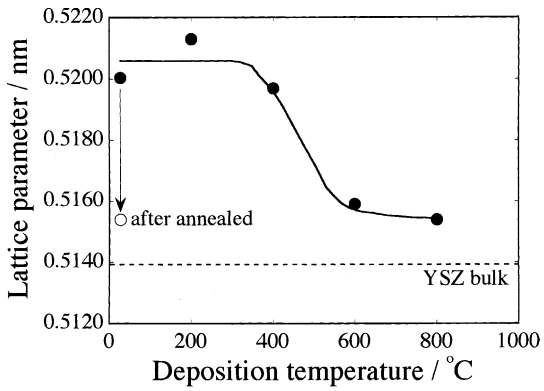


Fig. 4. Change of lattice parameter of YSZ thin films deposited on 800 °C deposited YSZ buffer layers with deposition temperature.

### 3.2. Proposal of conditions of epitaxial growth at room temperature from the point of crystal chemistry

Due to the fact that YSZ thin film was epitaxially grown on 800 °C deposited YSZ buffer layer at even 27 °C, the possibility of epitaxial growth was examined for several oxide ceramic materials. $CeO_2$ is identical crystal structure with YSZ (fluorite structure) and it was epitaxially grown at 27 °C as reported by Trik et al. [4,5]. $In_2O_3$ is c-rare structure. Since this structure is a kind of fluorite derivative, epitaxial growth was also expected. As the result, epitaxial $In_2O_3$ thin films was actually prepared at 27 °C. $Y_2O_3$ is also c-rare type structure, however, in this case, epitaxial $Y_2O_3$ thin films was not obtained and polycrystalline thin film was obtained at 27 °C. This discrepancy indicates that it is difficult to prescribe the epitaxial growth simply by crystal structure. $Y_2Ti_2O_7$ is pyrochlore structure. Though pyrochlore structure is another kind of fluorite derivative, it was impossible to obtain epitaxial thin film and amorphous film was obtained at 27 °C. MnZn-ferrite ($Mn_{0.22}Zn_{0.08}Fe_{0.70}O_4$) is spinel structure and it was epitaxially grown at 27 °C. This result agrees with the reports by Kiyomura and Gomi [7,8] that NiZn- and MnZn-ferrite thin films were epitaxially grown at room temperature. $TiO_2$ is rutile structure and $TiO_2$ thin film deposited on YSZ buffered Si(0 0 1) substrate was amorphous. We also tried to prepare epitaxial Pb(Zr,Ti)$O_3$, $SrTiO_3$, and $BaTiO_3$ on YSZ buffered Si(0 0 1) substrate at 27 °C, however, all films were amorphous. To interpret these results comprehensively, several plots were tried. As the parameters of plots, the degree of lattice mismatch between thin film materials and substrate (YSZ), number of components (number of cations) and electronegativity differences between cations and anions were employed in this work. The concept of electronegativity was first proposed by Pauling [10], however, it was prescribed for neutral atoms, and it was difficult to apply for ions with various valences. To overcome this difficulty, we adopted the electronegativity for different valence states of the element calculated by Martynov and Batsanov [11].

Fig. 5 shows the relationship between lattice mismatch and number of components. In this figure, closed circles denote that the material was epitaxially grown on YSZ buffered Si(0 0 1) substrate. Cross and closed triangles denote that the material was amorphous and polycrystal, respectively. Open circles denote the materials that epitaxial growth was reported in the literature. This figure shows the tendency that room temperature epitaxial growth occurs when lattice mismatch is close to zero. However, this consideration encounters two exceptions. One is exception for $Y_2Ti_2O_7$. The lattice mismatch between $Y_2Ti_2O_7$ and YSZ is small (−1.78%), however, this material became amorphous. Another exception is $Y_2O_3$. It should be remembered that $Y_2O_3$ was amorphous and $CeO_2$ was epitaxial on YSZ buffered Si(0 0 1) substrate. On the other hand, the lattice mismatch between $Y_2O_3$ and YSZ is 3.17% and this value is smaller than that between $CeO_2$ and YSZ (5.30%). Fig. 6 shows the relationship between electronegativity difference

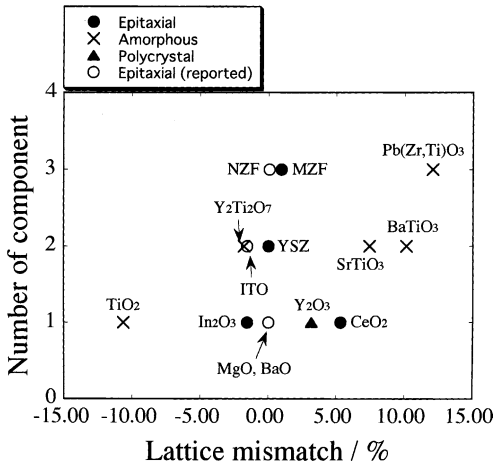


Fig. 5. Map of epitaxial growth at 27 °C from the point of number of component and lattice mismatch. YSZ: $ZrO_2$–$Y_2O_3$; MZF: (Mn,Zn)$Fe_2O_4$; NZF: (Ni,Zn)$Fe_2O_4$; ITO: $In_2O_3$–$SnO_2$.

and number of components (cations). This figure clearly explains our experimental results that all materials epitaxially grown on YSZ buffered Si(0 0 1) substrate had small electronegativity difference. By using this plot, the reason why $Y_2O_3$ was not epitaxially grown could be ascribed to large electronegativity difference. This consideration suggests that materials with high covalent bonding character tend to be epitaxially grown. However, for this plot, we have encountered another difficulty that preparation of epitaxial BaO and MgO thin films have been reported in the literature [2,6] though these materials have high electronegativity difference (high ionic bonding character). It should be noted that epitaxial MgO film deposited at low temperature has been deposited on MgO(0 0 1) substrate [2], therefore, this epitaxial growth is homoepitaxial and the lattice mismatch was 0.0%. The epitaxila BaO film deposited at room temperature has been deposited on $SrTiO_3$(0 0 1), therefore,

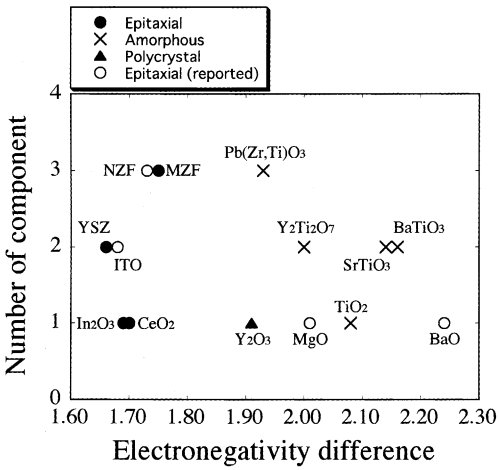


Fig. 6. Map of epitaxial growth at 27 °C from the point of number of component and electronegativity difference. YSZ: $ZrO_2$–$Y_2O_3$; MZF: (Mn,Zn)$Fe_2O_4$; NZF: (Ni,Zn)$Fe_2O_4$; ITO: $In_2O_3$–$SnO_2$.

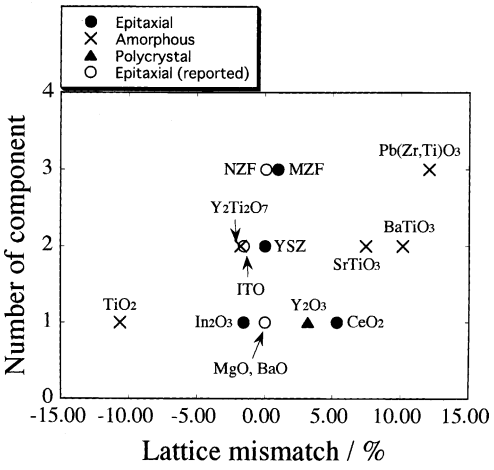


Fig. 7. Map of epitaxial growth at 27 °C from the point of electronegativity difference and lattice mismatch. YSZ: $ZrO_2$–$Y_2O_3$; MZF: $(Mn,Zn)Fe_2O_4$; NZF: $(Ni,Zn)Fe_2O_4$; ITO: $In_2O_3$–$SnO_2$.

the lattice mismatch was 0.0% if 45° rotation epitaxial configuration was postulated. In addition, we will also ascribed the reason of epitaxial growth of MgO and BaO to the fact that these materials are composed of only one kind of cation. By these considerations, the relationship between lattice mismatch and electronegativity difference was also plotted (Fig. 7). This figure clearly indicates that those materials with both small lattice mismatch and small electronegativity difference are epitaxially grown even at low temperature. In addition to this condition, those materials with small lattice mismatch and composed of single component could be epitaxially grown even at low temperature.

On the basis of our results and reported results, the conditions of epitaxial growth at even low temperature is summarized as following:

(1) Materials with both small lattice mismatch and small electronegativity difference; or
(2) Materials with small lattice mismatch and composed of single component.

From these considerations, it is expected that it would be difficult to realize epitaxial growth of materials with perovskite structure at room temperature. Therefore, somewhat substrate heating would be needed for perovskite structure material to realize epitaxial growth. However, it is expected that the minimum crystallization temperature of $Pb(Zr,Ti)O_3$ would be lower than that of $SrTiO_3$ and $BaTiO_3$ because electronegativity difference of $Pb(Zr,Ti)O_3$ is smaller than that of $SrTiO_3$ and $BaTiO_3$. The proposed conditions will helpful to design epitaxial growth of oxide ceramic thin film at low temperature.

## 4. Conclusions

Preparation of epitaxial oxide ceramic thin film at room temperature was examined. Epitaxial YSZ thin films was succeeded to prepare at room temperature (27 °C) by use of nm thick YSZ buffer layer deposited at 800 °C on Si(0 0 1) substrate. Room temperature epitaxial growth of YSZ was realized on 0.8 nm thick ultra thin YSZ buffer layer, however, to achieve high crystallinity, 6.7 nm thick was needed. On the 6.7 nm thick YSZ buffered Si(0 0 1) substrate, we have tried to prepare epitaxial oxide ceramic thin films. As the result, epitaxial $CeO_2$, $In_2O_3$, and MnZn-ferrite thin films were successfully deposited even at room temperature. The conditions of epitaxial growth at such low temperature was considered from the point of crystal chemistry. As the result, following conditions were proposed:

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