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Epitaxial Growth of Ceramic Layers by Laser MBE

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The growth modes of oxide films on Si by ultra-high vacuum (UHV) laser ablation was investigated by reflection high energy electron diffraction (RHEED) and X-ray photoelectron spectroscopy (XPS). Coulombic interaction between the film depositing species and the atoms on the substrate surface is presumed to dominate the film orientation. Epitaxial layer-by-layer growth was achieved for CeO_2(111) film on Si(111) substrate.

1. INTRODUCTION

Epitaxial growth of ceramic thin films on Si attracts our interest as a basic technology for fabricating devices composed of ceramics and Si as well as for constructing layered ceramics on Si. For the deposition of oxide films on Si, we have to compromise such contradicting process parameters as UHV or reducing atmosphere to prevent the oxidation of Si surface and presence of oxygen sufficient for giving the desired oxidation state in the ceramic film. It is well known that the laser ablation deposition is a useful method for converting ceramic targets into films. Although the conventional processes use relatively high oxygen pressures ($\leq$10Torr), oxidized films could be deposited even in UHV either when the target materials have high oxygen affinity[1)] or when low pressure oxidizing species are chemically activated.[2)]

We describe, in this paper, our concept about the growth mechanism of ceramic films based on the epitaxial growth of CeO_2 and $SrTiO_3$ on Si. These ceramics have oxygen affinity high enough to achieve almost stoichiometric compositions in UHV[3)] as well as lattices matched well with Si. Two-dimensional layer-by-layer growth of ceramic films via the laser ablation in UHV is also reported.

2. EXPERIMENTAL PROCEDURES

Si substrates were cleaned by the conventional method using chemical etching, UV irradiation[4)], and heating in the UHV deposition chamber. ArF excimer laser of about 1J/cm^2 was irradiated on a sintered CeO_2 or $SrTiO_3$ target at 2Hz. Films were deposited at a pressure below 1×10^{-8} Torr and at a substrate temperature between 600 and 800°C.

During the deposition, in-situ RHEED was recorded by using a CCD video camera. The crystallinity and chemical state of the film were

Table I Film orientations prepared by the laser MBE method at Tsub.$\geq$600°C for CeO_2 films and Tsub.$\geq$700°C for $SrTiO_3$ (STO) films.

Film	Substrate	Orientation	
CeO_2	Si-O/Si	$CeO_2(111)$	in-plane random
	Si(001)	$CeO_2(110)//Si(001)$	$CeO_2[1\bar{1}0]//Si[110]$ & $CeO_2[001]//Si[110]$
	Si(110)	$CeO_2(111)//Si(110)$	$CeO_2[01\bar{1}]//Si[1\bar{1}0]$
	Si(111)	$CeO_2(111)//Si(111)$	$CeO_2[11\bar{2}]//Si[11\bar{2}]$
	STO(001)	$CeO_2(001)//STO(001)$	$CeO_2[110]//STO[010]$
STO	Si(001)	STO(001)//Si(001)	STO[010]//Si[110]
	STO(001)	STO(001)//STO(001)	STO[010]//STO[010]

determined by ex-situ XRD and in-situ XPS, respectively.

3. RESULTS AND DISCUSSION

3-1. *Growth of CeO_2 and $SrTiO_3$ Films on Si Substrates*

Table I summarizes the growth behavior of CeO_2 and $SrTiO_3$ films on Si and $SrTiO_3$ single crystals. The RHEED observation showed that the critical temperatures for the growth of single crystal films were about 600°C for CeO_2 and 700°C for $SrTiO_3$ under the conditions of this study. The epitaxial CeO_2 films were obtained on Si(111) and $SrTiO_3$(001), but not on Si(001) and Si(110).

These results can be understood qualititavely by considering the atomic arrangement at the interfaces. Asuming that CeO_2 and $SrTiO_3$ are primarily fragmented into oxides of mono- or di-atomic metals in the gas phase, the oxygen part are presumed to cover the clean Si surface in the initial stage of the deposition. A preliminary discussion was made for the case of CeO_2 film growth on Si in our previous paper.$^{1)}$

The interaction at the interface was investigated by in-situ XPS. Figure 1 shows the result of CeO_x-(110)/Si(001) interface. Increase of binding energy of Ce 3d 5/2 and decrease of $4f^0$ satellite peak height were observed for the photoelectrons emerging from the film within 1nm thick from the interface with Si, indicating that Ce was partially reduced from Ce^{4+} to Ce^{3+} at the interface.

3.2 *Layer-by-Layer Growth of CeO_2-(111) on the Si(111) Substrates*

Recently, RHEED intensity oscillation was observed during the epi-

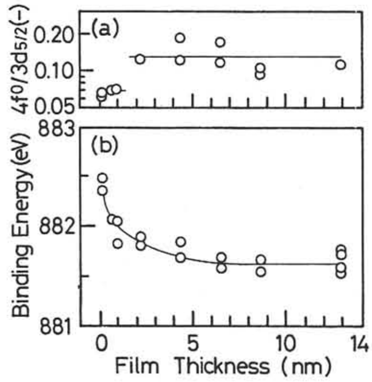

Fig.1 Relatonship between XPS peaks of Ce 3d and thickness of the film deposited at 600°C on Si(001). (a) Variation of the peak height of $4f^0$ satellite of 3d 3/2 relative to that of 3d 5/2. (b) Variation of binding energy of 3d 5/2.

taxial growth of ceramic films on SrTiO$_3$ substrates by a reactive evaporation by Terashima et al.$^{5)}$ We also observed RHEED intensity oscillations in epitaxial growth of ceramics as shown in Fig.2. This provides the first definite evidence for ceramics heteroepitaxy on Si substrate by the laser MBE. The oscillation periodicity of 0.32nm calculated from the deposition rate agreed well with the interplane distance of CeO$_2$(111) of 0.312nm. These results indicate the layer-by-layer growth of CeO$_2$ on clean Si(111) surface, as visualized in Fig.3.

Figure 4 shows the result of grazing angle XRD on the epitaxial CeO$_2$ film on Si(111). Three-fold and six-fold symmetries of measured (113) and (420) peaks around <111> axis show that the film is single crystal without twins.

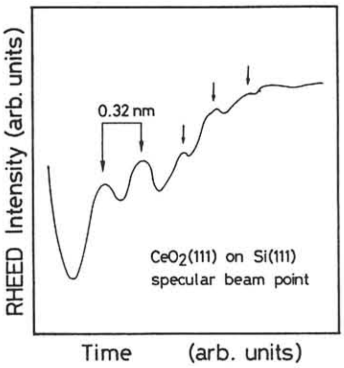

Fig.2 Typical RHEED intensity oscillations during CeO$_2$(111) growth on Si(111) at 650°C. Azimuth was [11$\bar{2}$] for the (111) surface.

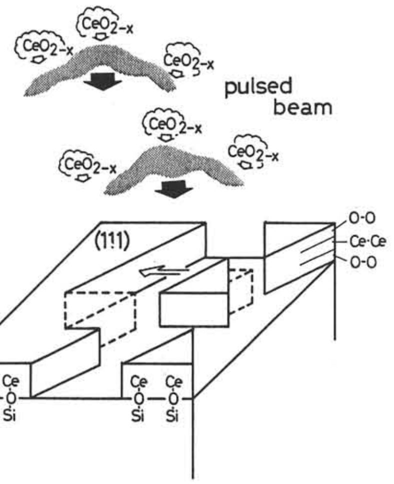

Fig.3 A schematical illustration for the growth process of CeO$_2$(111) on Si(111) clean surface.

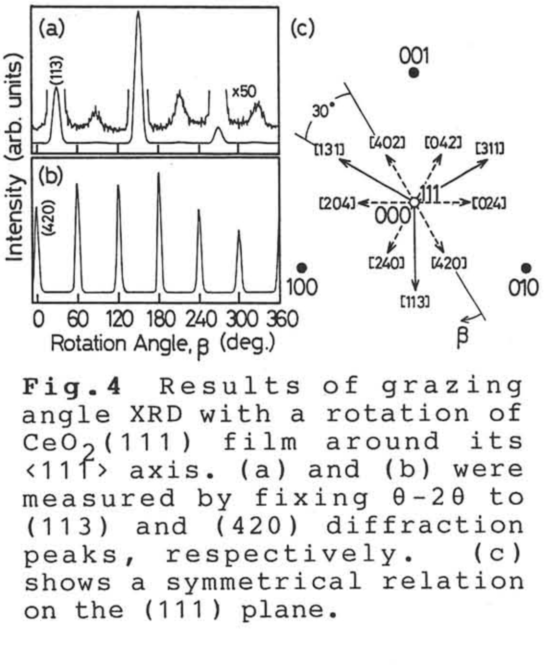

Fig.4 Results of grazing angle XRD with a rotation of CeO$_2$(111) film around its <111> axis. (a) and (b) were measured by fixing θ-2θ to (113) and (420) diffraction peaks, respectively. (c) shows a symmetrical relation on the (111) plane.

3-3. *Hetero-Epitaxial Growth of CeO$_2$(001) on Si(001)*

CeO$_2$(001) plane can be useful for successive epitaxial growth of other perovskite structures on it. The epitaxial growth of CeO$_2$(001) on Si(001) was reported by Inoue et al$^{6)}$, but it has been unsuccessful in our study. The preferential bond formation between the oxygens on CeO$_2$(001) plane and the dangling bonds on Si(001) could prevent the epitaxial growth.$^{1)}$ To overcome this difficulty, the insertion of a layer which can interconnect Si(001) with CeO$_2$(001) should be effective. We examined this

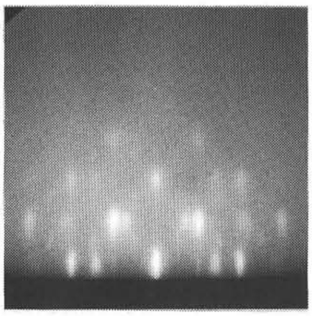

Fig.5 Typical RHEED pattern of double domained $CeO_2(110)$ film deposited on Si(001) clean surface at 650°C. Azimuth was [110] for Si(001).

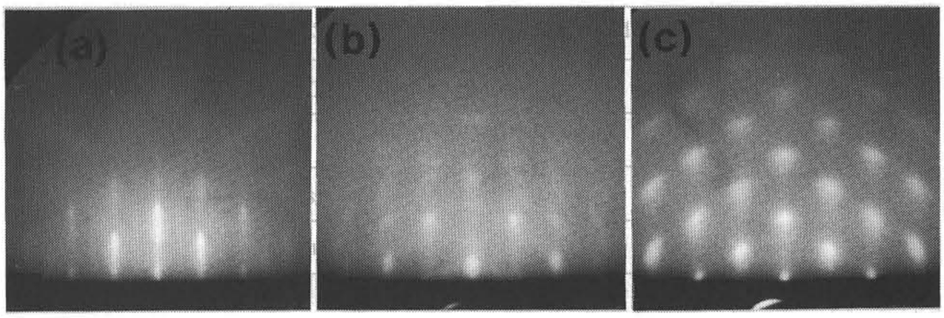

Fig.6 Typical RHEED patterns of (a) Si(001) clean surface, (b) $SrTiO_3(001)$ deposited on Si(001) at 750°C, and (c) $CeO_2(001)$ deposited on $SrTiO_3(001)$ at 650°C. All azimuths were the same: [110] for Si(001).

possibility by using $SrTiO_3(001)$ as the interlayer.

Figure 5 shows the RHEED pattern of CeO_2 grown at 650°C without $SrTiO_3$ interlayer in [110] azimuth for Si(001). Figure 6 shows in-situ RHEED patterns of (a) the initial Si(001) surface, (b) the $SrTiO_3$ interlayer at 750°C, and (c) the CeO_2 film in the same azimuth with Fig.5. The desired orientation of $CeO_2(001)//SrTiO_3(001)//Si(001)$ and $CeO_2[110]//SrTiO_3[010]//Si[110]$ were achieved, although the rocking curve of $CeO_2(002)$ was not so sharp (FWHM=3.3°).

4. CONCLUSIONS

Layer-by-layer epitaxial growth of $CeO_2(111)$ on Si(111) was verified by the observation of RHEED intensity oscillation during the film deposition by the laser MBE. On Si(001), $CeO_2(110)$ was grown instead of the epitaxial (001) growth. The use of $SrTiO_3$ as an interlayer on Si(001) was effective for facilitating the epitaxial growth of $CeO_2(001)$.

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REFERENCES

1) M.Yoshimoto, H.Nagata, T.Tsukahara, and H.Koinuma; to be published in *Jpn. J. Appl. Phys* **29**(1990).
2) D.G.Schlom, A.F.Marshall, J.T.Sizemore, Z.J.Chen, J.N.Eckstein, I.Bozovic, K.E.von Dessonneck, J.S.Harris, Jr. and J.C.Bravman; to be published in *J.Cryst. Growth*..
3) O.T.Sorensen; *J. Solid State Chem.* **18**(1976)217.
4) T.Kaneko, M.Suemitsu, and N.Miyamoto; *Jpn. J. Appl. Phys.* **28**(1989) 2425.
5) T.Terashima, Y.Bando, K.Iijima, K.Yamamoto, K.Hirata, K.Hayashi, K.Kamigaki, and H.Terauchi; submitted to *Phys. Rev. Lett.*.
6) T.Inoue, Y.Yamamoto, S.Koyama, S.Suzuki, and Y.Ueda; *Appl. Phys. Lett.* **56**(1990)1332.