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Preparation of Epitaxial $SrRuO_3$ Thin Film by Metalorganic Chemical Vapor Deposition

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$SrRuO_3$ is a promising electrode material for ferroelectric memories. We firstly succeeded in the preparation of $SrRuO_3$ films on (100)$SrTiO_3$, (100)$LaAlO_3$ and (100)MgO substrates by metalorganic chemical vapor deposition (MOCVD) using $Sr(C_{11}H_{19}O_2)_2(C_8H_{23}N_5)_2$, $Ru(C_{11}H_{19}O_2)_3$ and O_2 as source materials. It turned out that the growth of $SrRuO_3$ thin film by MOCVD had composition self-limiting under the excess $Ru(C_{11}H_{19}O_2)_3$ gas concentration, i.e., Ru/(Ru+Sr) ratio was saturated to be 0.5. $SrRuO_3$ thin films were epitaxially grown with (100) orientation at 750 ℃ on all kinds of substrates. The lattice constant was about 0.393 nm regardless of the kinds of substrates. The resistivity was also almost the same as that of the single crystal, 0.28 mΩ・cm regardless of the kinds of substrates above 600 ℃.
Key words:$SrRuO_3$, MOCVD, epitaxial, resistivity, deposition mechanism

1.INTRODUCTION

Ferroelectric thin films have been widely studied because of its application to nonvolatile memories. $Pb(Zr,Ti)O_3$ and Bi-layered ferroelectric such as $Bi_4Ti_3O_{12}$ and $SrBi_2Ta_2O_9$, has been widely investigated. These ferroelectric have a structure based on the perovskite-type of structure. On the other hand, it has been known that the properties of ferroelectric memory changed by a substance of bottom electrode. Moreover, it is known to be improved by using oxide bottom electrode instead of widely-used Pt.

$SrRuO_3$ (SRO) is a conductive oxide with high thermal stability and high resistance to chemical corrosion. In addition, it has the same perovskite-type of structure as ferroelectric oxide and specially lower resistivity in conductive oxides having this structure. Moreover, this material has a good lattice matching with ferroelectric materials. Epitaxially grown SRO thin films were reported to be deposited on (100)$SrTiO_3$,[1-7] (100)$LaAlO_3$[7-9] and (100)MgO[2,6] substrates by sputtering,[1-3] pulsed laser deposition,[5-9] and so on. However no studies have been reported for the preparation of epitaxial SRO thin films by chemical vapor deposition (CVD) which was often used to prepare ferroelectric thin film.

In the present study, we successfully prepared SRO thin films by metalorganic CVD (MOCVD) and investigated the crystallinity, the morphology and the resistivity of the film. Moreover, the deposition mechanism was discussed.

2.EXPERIMENTAL

SRO thin films were prepared by MOCVD using $Sr(C_{11}H_{19}O_2)_2(C_8H_{23}N_5)_2$, $Ru(C_{11}H_{19}O_2)_3$ and O_2 as source materials. A vertical cold-wall type reactor was used for the deposition. The apparatus used in the present study was almost the same used for Y_2O_3-stabilized ZrO_2 (YSZ) preparation.[10]

The vapor of $Ru(C_{11}H_{19}O_2)_3$ was generated by passing N_2 gas over a heated solid source. On the other hand, the vapor of $Sr(C_{11}H_{19}O_2)_2(C_8H_{23}N_5)_2$ source was generated by bubbling N_2 gas including $C_8H_{23}N_5$ gas through a heated liquid source. Single crystals of (100)$SrTiO_3$, (100)$LaAlO_3$ and (100)MgO were used as substrates. The estimated mismatches between the SRO and (100)$SrTiO_3$, (100)$LaAlO_3$ and (100)MgO substrates at room temperature are 0.6 %, 3.7 % and -6.6 %, respectively. The detailed deposition conditions are summarized in Table. I. The theoretical input gas concentration was defined as R[source][10]

The crystallinity of the SRO thin films were characterized by X-ray diffraction (XRD) using CuK_α line. The resistivity of the SRO thin films was measured using a standard four-probe technique. The composition of the films and the

Table. I Deposition conditions of $SrRuO_3$ film

Deposition temperature	500～750 ℃	
Reactor pressure	1.3 kPa	
Organometallic (OM) precursor temperature	$Sr(C_{11}H_{19}O_2)_2(C_8H_{23}N_5)_2$	135 ℃
	$Ru(C_{11}H_{19}O_2)_3$	115～135 ℃
Pressure of OM precursor vaporizer	$Sr(C_{11}H_{19}O_2)_2(C_8H_{23}N_5)_2$	27 kPa
	$Ru(C_{11}H_{19}O_2)_3$	24 kPa
Total gas flow rate	600 cm^3/min	
Flow rate of O_2 gas	300 cm^3/min	
Substrates	(100)$SrTiO_3$, (100)$LaAlO_3$, (100)MgO single crystals	
Film thickness	50～150 nm	
Deposition rate	0.5～1.4 nm/min	

surface morphology were investigated using fluorescent X-ray (XRF) and scanning electron microscopy (SEM), respectively

3.RESULTS AND DISCUSSION

Fig.1 shows the deposition temperature dependency of the degree of the orientation for thin films on (100)$SrTiO_3$, (100)$LaAlO_3$ and (100)MgO substrates. The degree of (h00) orientation was defined from the XRD pattern as the ratio of the summation of the intensities of (h00) diffraction to that of (hkl) ones, Σ [I(h00)]/ Σ [I(hkl)]. The degree of (h00) orientation increased with increasing deposition temperature and reached to the 100 %, perfect (100) orientation, at 750 ℃ on all kinds of substrates. Moreover, the films on smaller lattice mismatch substrate took higher degree of (100) orientation at 600-700 ℃.

Fig.2 shows the deposition temperature dependency of the resistivity, ρ, of the film measured at room temperature using four-probe method. The resistivity was high at 500 ℃ and decreased with increasing deposition temperature and reached to the almost constant value above 600 ℃. This value was almost the same as reported value for the single crystal, 0.28 mΩ・cm.[11] This result is in agreement with Q.X. Jia, et al.[6] reports for the film deposited by sputtering. Moreover, the deposition temperature dependency of ρ was irrespective of the kinds of the substrate.

Fig.3 shows the relationship between the Ru/(Sr+Ru) ratio and the input gas concentration of $Ru(C_{11}H_{19}O_2)_3$, $R[Ru(C_{11}H_{19}O_2)_3]$ under constant input gas concentration of $Sr(C_{11}H_{19}O_2)_2(C_8H_{23}N_5)_2$, $R[Sr(C_{11}H_{19}O_2)_2(C_8H_{23}N_5)_2]$ at 750 ℃. The Ru/(Sr+Ru) ratio took same value regardless of the kinds of substrates. The Ru/(Sr+Ru) ratio increased with increasing $R[Ru(C_{11}H_{19}O_2)_3]$ and reached to the almost constant value, 50 mol%, above 1.9×10^{-2} cm^3/min. This result shows that the growth of SRO thin film by CVD had composition self-limiting. The reason was considered as following; The RuO_2 film was not deposited at 750 ℃ from

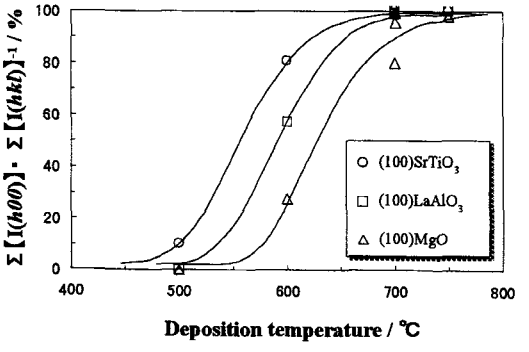

Fig.1 The deposition temperature dependency of the degree of orientation for thin films on (100)$SrTiO_3$, (100)$LaAlO_3$, (100)MgO substrates.

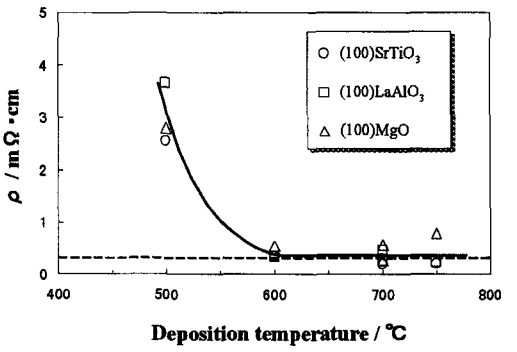

Fig.2 The deposition temperature dependency of the resistivity, ρ, measured at room temperature. The broken line indicates the reported value for the single crystal, 0.28mΩ・cm.

$Ru(C_{11}H_{19}O_2)_3$-O_2 system, because of its high vapor pressure. Therefore the excess Ru atom is not considered to be deposited as RuO_2 film when the Sr-Ru-O film was deposited. On the other hand, Ru atoms combined with Sr atoms made SRO phase and were deposited at higher temperature due to the low vapor pressure of Ru atom from SRO phase. As result, it is considered that the Ru/(Sr+Ru) ratio kept the almost constant value, 50 mol%.

Fig.4 shows XRD patterns of a SRO films at 750 ℃. Only (h00) peaks of SRO phase was observed together with the peaks of substrates. Therefore, the SRO thin films at 750 ℃ on all kinds of substrate were ascertained to be grown with perfect (h00) orientation as shown in Fig.1.

Epitaxial relationship between the film and substrate was ascertained by X-ray pole figure measurement. As a result, The SRO thin films on all kinds of substrate were epitaxial growth at 750 ℃.

Fig.5 shows the rocking curves of (200) reflection of SRO thin films deposited at 750 ℃. The full width at half maximum(FWHM) of (200) peak of SRO were 0.046 ° , 0.729 ° and 1.011 ° for $SrTiO_3$, $LaAlO_3$ and MgO substrates, respectively. On the other hand, the FWHM of (200) peak of $SrTiO_3$, $LaAlO_3$ and MgO were 0.008 ° , 0.010 ° and 0.010 ° , respectively. This shows that FWHM of SRO is mainly determined by the lattice mismatch between the film and substrate; the value of FWHM of SRO is small in the case of smaller lattice mismatch.

The surface morphologies of the epitaxial SRO thin films deposited on different substrates are shown in Fig.6. The surface became smooth when the lattice mismatch was small. As a result, small mismatch substrate, (100)$SrTiO_3$, is suitable for the epitaxially grown SRO film preparation with high orientation and smooth surface.

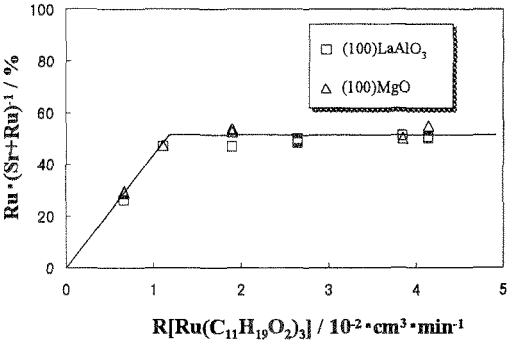

Fig.3 The relationship between the $Ru \cdot (Sr+Ru)^{-1}$ ratio and $R[Ru(C_{11}H_{19}O_2)_3]$ at 750 ℃.

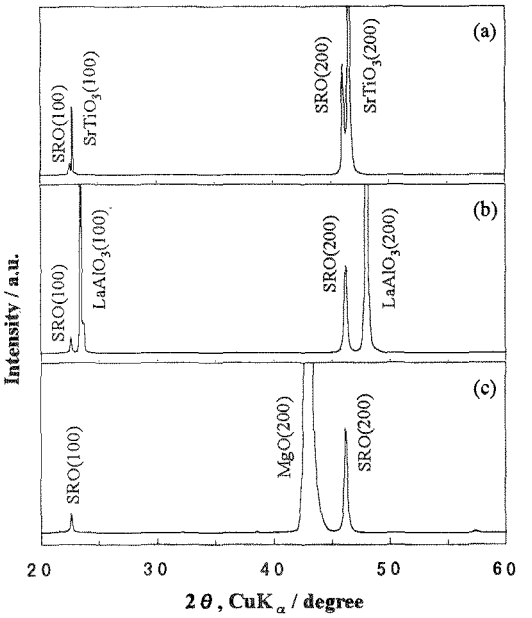

Fig.4 XRD patterns of the SRO thin films at 750℃ on (a) $SrTiO_3$ (b)$LaAlO_3$ (c) MgO substrates.

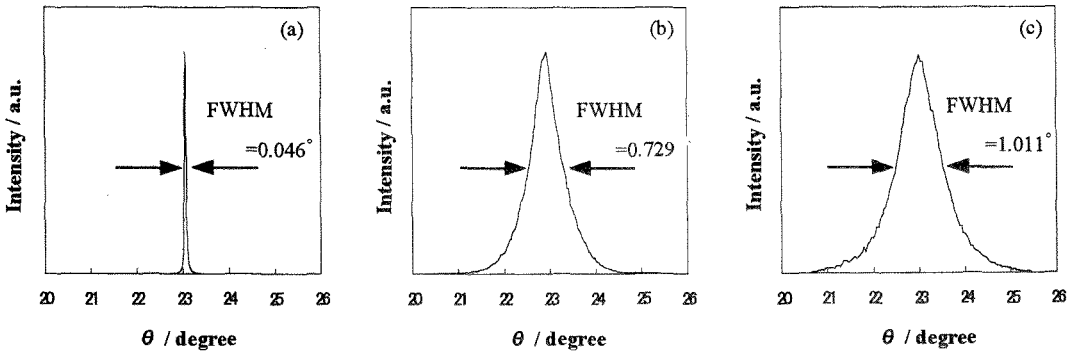

Fig.5 The rocking curves of (200) diffraction of the SRO thin films deposited at 750℃ on (a) $SrTiO_3$ (b)$LaAlO_3$ (c) MgO substrates, respectively. FWHM of (200) peak of $SrTiO_3$, $LaAlO_3$, and MgO were 0.008°, 0.010° and 0.010°,respectively.

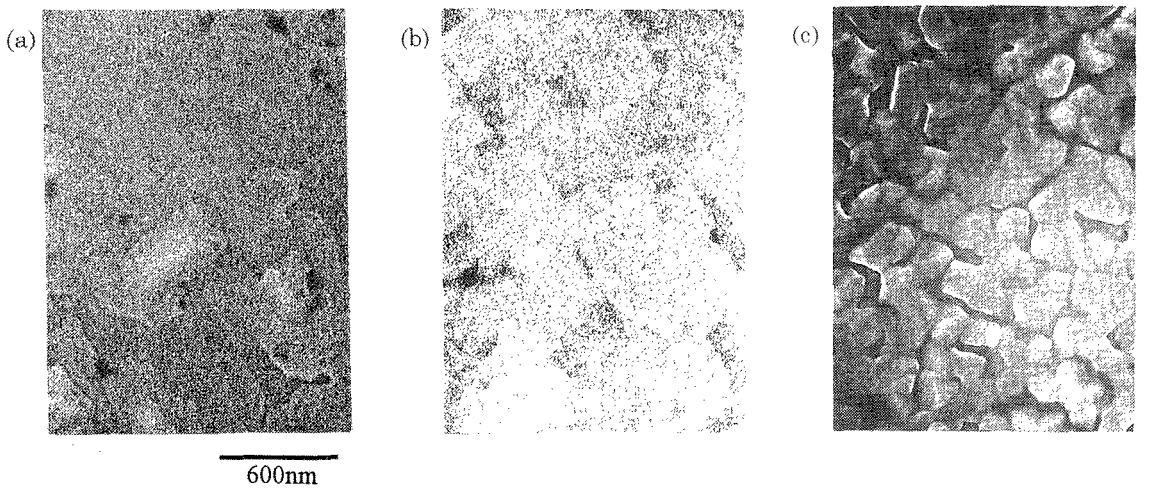

Fig.6 SEM photographs of the SRO thin films deposited at 750°C on (a) $SrTiO_3$ (b)$LaAlO_3$ (c) MgO substrates.

4.CONCLUSION

It turned out that the growth of SRO thin film by CVD had composition self-limiting. The crystallinity of the SRO thin films was closely related to the kinds of substrate and deposition temperature. SRO thin films on smaller lattice mismatch substrate and at higher deposition temperature took higher degree of orientation. Moreover, the SRO thin films on smaller lattice mismatch substrate had smoother surface morphology. The resistivity of the SRO thin films was a function of deposition temperature but was not independent of the kinds of substrate.

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