$SrRuO_3$ thin films grown on MgO substrates at different oxygen partial pressures

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A comprehensive study of $SrRuO_3$ thin films growth on (001) MgO substrates by pulsed laser deposition in a wide oxygen pressure range from 10 to 300 mTorr was carried out. The experimental results showed a correlation between the lattice constants, resistivity, and oxygen partial pressures used. Ru deficiency detected only in films deposited at lower oxygen pressures (<50 mTorr), resulted in an elongation of the in-plane and out-of-plane lattice constants and an increase in the film resistivity. When deposited with oxygen partial pressure of 50 mTorr, $SrRuO_3$ films had lattice parameters matching those of bulk $SrRuO_3$ material and exhibited room temperature resistivity of 320 μΩ·cm. The resistivity of $SrRuO_3$/MgO films decreased with increasing oxygen partial pressure.

I. INTRODUCTION

$SrRuO_3$ is a ferromagnetic metal oxide with outstanding thermal conductivity, stability, and high resistance to chemical erosion.[1–3] Thin films of $SrRuO_3$ have been widely used as a buffer layer for developing superconducting $YBa_2Cu_3O_{7-\delta}$ films[3] and as a conducting electrode for ferroelectric capacitors.[4–6] At room temperature, $SrRuO_3$ exhibits orthorhombic perovskite structure with lattice constants $a = 5.56$ Å, $b = 5.55$ Å, and $c = 7.86$ Å,[3,7] which can also be described as a pseudocubic perovskite structure with lattice constants of $a = 3.93$ Å.[3,8] With increasing temperature, the orthorhombic structure transforms into a tetragonal structure at 547 °C and subsequently transforms into a cubic structure at higher temperature (at 677 °C).[9,10] Polycrystalline $SrRuO_3$ has a resistivity of around 1130 μΩ·cm, whereas the resistivity of single crystalline $SrRuO_3$ is around 280 μΩ·cm at room temperature.[11]

The microstructural and electrical properties of $SrRuO_3$ thin films strongly depend on the deposition conditions. Substrate temperature and oxygen pressure are of prime importance when pulsed laser deposition (PLD) is used. Epitaxial $SrRuO_3$ thin films have been successfully grown by PLD on various single crystal substrates, such as $SrTiO_3$,[11–19] $LaAlO_3$,[7,20–22] and MgO.[1,23] When $SrRuO_3$ is deposited on (001) $SrTiO_3$ substrate, film can grow epitaxially with [001], [110] or [1$\bar{1}$0] planes parallel to the $SrTiO_3$ surface, which leads to six possible $SrRuO_3$ domain structures and orientations.[13,16] The domain structures of $SrRuO_3$ films grown on $LaAlO_3$ substrates are different from those grown on $SrTiO_3$. $SrRuO_3$ thin films on (001) $LaAlO_3$ substrate consist of all three types of the orientation domains, which are randomly distributed in the film.[23] In contrast to the atomically flat surface of $SrRuO_3$ films on $SrTiO_3$ substrate, the $SrRuO_3$ film grown on $LaAlO_3$ substrate has a rough surface with a sinusoidal-like modulation. The reason for these differences was ascribed as an effect of lattice mismatch across the film–substrate interface.[22] Zakharov et al.[11] have shown that $SrRuO_3$/$SrTiO_3$ films deposited at 775 °C and 200 mTorr O_2 pressure exhibit a low resistivity of 150 μΩ·cm because of the favorable combination of substrate temperature and oxygen pressure. The resistivity of $SrRuO_3$/$LaAlO_3$ films decreases with increasing deposition temperature due to the improved crystallinity of the films grown at higher temperatures.[7,23] The $SrRuO_3$/$LaAlO_3$ films grown at 775 °C and 200 mTorr O_2 pressure show a room temperature resistivity of 280 μΩ·cm.[23] The resistivity of $SrRuO_3$ increases as the oxygen pressure during growth is decreased due to the disordering and lattice imperfections.[24]

To grow $SrRuO_3$ epitaxially on single crystal substrate, less lattice mismatch between the in-plane lattice parameter of $SrRuO_3$ and that of a substrate is required. The strain introduced by the residual lattice mismatch can affect the structural and electrical properties of the $SrRuO_3$ films. The most common choice of substrates for growing $SrRuO_3$ thin films are $SrTiO_3$ and $LaAlO_3$ because of their best lattice mismatch (0.6% for $SrRuO_3$ on $SrTiO_3$ and 1.7% for $SrRuO_3$ on $LaAlO_3$). However, the high relative dielectric constant ($\varepsilon \approx 300$ at 300 K) of $SrTiO_3$ and tendency to form crystallographic defects [e.g., twin planes along (100)] on $LaAlO_3$ limit their applications particularly in microwave devices. For such application, MgO substrate ($\varepsilon \approx 10$ at 300 K; $\tan\delta \approx 10^{-5}$) is more preferable even though the lattice mismatch between MgO and $SrRuO_3$ is relatively

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larger (~6.7%). Several $SrRuO_3$ films were grown on MgO at various oxygen partial pressures and temperatures. However, (00*l*)- or (*h*00)-oriented $SrRuO_3$ films have not been obtained at O_2 pressure below 150 mTorr.[3] Furthermore, none of the reported XRD studies on $SrRuO_3$/MgO films presented the XRD pattern above 2θ of 55°. This leads to a question whether $SrRuO_3$/MgO films are single crystalline films as an additional peak appears at 2θ of 55°.

Although significant knowledge has been gained on the microstructure of epitaxial $SrRuO_3$ films grown on $SrTiO_3$ and $LaAlO_3$ substrates, there is still no comprehensive study of the $SrRuO_3$ growth process on MgO substrate and especially about the effect of the oxygen partial pressure. Therefore, this paper reports on the impact of the oxygen partial deposition pressure on the structural and electrical properties of $SrRuO_3$ thin films grown on MgO substrates.

II. EXPERIMENTAL

$SrRuO_3$ thin films were grown on single crystal (001)-oriented MgO substrates by PLD using a KrF excimer laser (λ = 248 nm). A stoichiometric single-phase $SrRuO_3$ target was ablated with a laser beam fluency of 0.8 J/cm^2 at 8 Hz. During the deposition, the MgO substrates were kept at a temperature between 650 and 750 °C. The oxygen partial pressure was in the range from 10 to 300 mTorr. Subsequent to the PLD process, as-grown films were in situ post-annealed for 20 min at the deposition temperature and 700 Torr oxygen pressure and then slowly (10 °C/min) cooled down to room temperature. The target-to-substrate distance (50 mm) and laser fluency were optimized for $SrRuO_3$ thin films deposition.

The crystalline structure of these thin films was investigated by x-ray diffraction (XRD) and scanning electron microscopy (SEM). The out-of-plane lattice parameters were evaluated out of θ–2θ scans performed from 20° to 120° in the Bragg–Brentano configuration, while the in-plane lattice parameters were evaluated by grazing incidence XRD. These evaluation procedures are presented in detail elsewhere.[25] The phase composition was investigated using an Oxford Instruments energy dispersive x-ray (EDX) analysis system (Oxford Instruments PLC, Oxfordshire, UK) attached to the SEM. The resistivity of the films was evaluated by a standard four-point probe method using Agilent B1500A semiconductor analyzer (Agilent Technologies UK Ltd., Santa Clara, CA) attached to a Signatone manual probe station (Signatone Corporation, Gilroy, CA).

III. RESULTS AND DISCUSSION

As shown in Fig. 1, the $SrRuO_3$ film deposited on MgO at 650 °C and 100 mTorr O_2 was amorphous. Crystalline $SrRuO_3$ films were obtained when the deposition temperature was 700 °C or above. However, at higher deposition temperature of 750 °C, an additional peak was observed at 2θ of 57.3°, which was indexed as (112) peak. This additional peak may originate from the twin growth of $SrRuO_3$ film, which has been reported. The twin formation during the $SrRuO_3$ film growth depends strongly

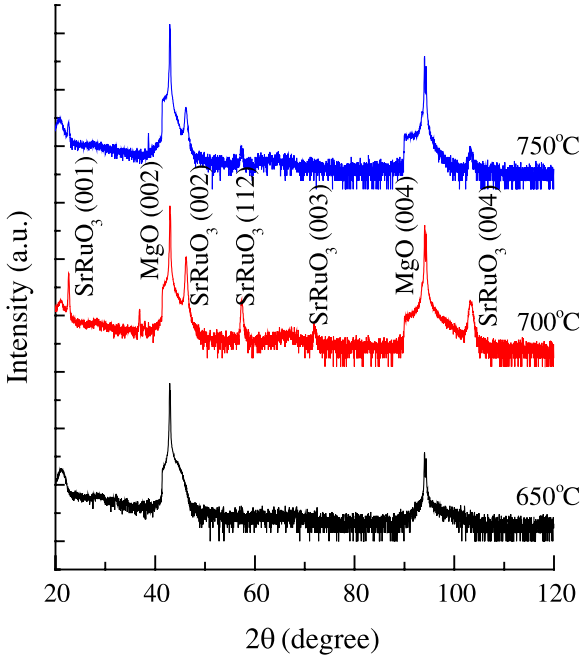


FIG. 1. XRD patterns of $SrRuO_3$ thin films deposited on MgO (001) substrates at 100 mTorr and different temperatures.

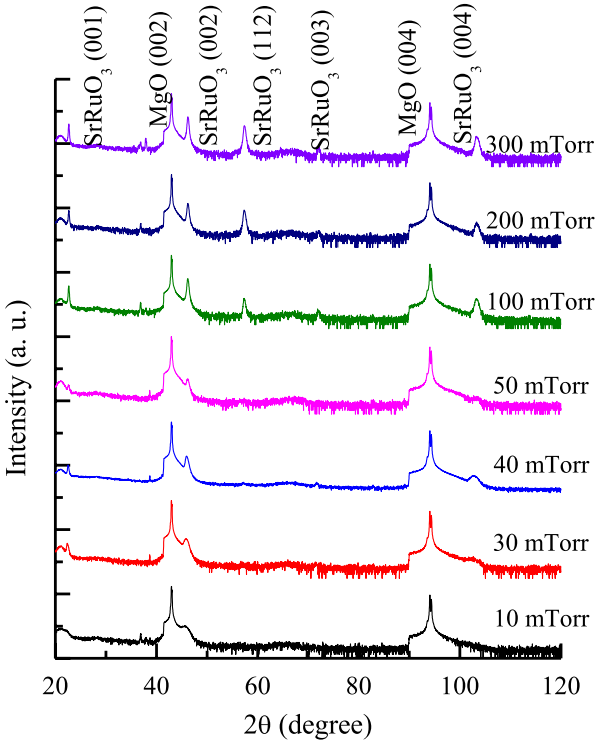


FIG. 2. XRD patterns of $SrRuO_3$ thin films on MgO (001) substrate deposited over a range O_2 pressure from 10 to 300 mTorr.

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upon the growth conditions (substrate temperature and oxygen partial pressure) and miscut angle of the substrate.[11,12] Up to our knowledge, presence of this peak was not reported before (all previous studies reported XRD patterns of $SrRuO_3$/MgO films only up to 2θ of 55°). Appearance of this additional peak can be suppressed by reducing the O_2 partial pressure and will be further discussed hereinafter. Figure 2 shows the XRD patterns for the $SrRuO_3$ thin films deposited at temperature of 700 °C and oxygen partial pressures varied from 10 to 300 mTorr. For simplicity, the peak indexes and the subsequent lattice constant evaluation were based on the consideration of the pseudocubic structure of $SrRuO_3$. As one can see, the first evidence (i.e., XRD peaks) of crystalline $SrRuO_3$ films growth appeared at O_2 partial pressure of 10 mTorr. As the O_2 partial pressure increased above 30 mTorr, the intensities of the $SrRuO_3$ corresponding XRD peaks increased, while their full-width at half-maximum (FWHM) decreased, as can be seen in Fig. 3. The value of FWHM from the ω-rocking curve on (002) $SrRuO_3$ reflection decreases monotonically with the increasing of the O_2 partial pressure except the value of FWHM at 50 mTorr. This implies that the increase of O_2 partial pressure improves the $SrRuO_3$ film crystalline perfection and promotes preferential (00*l*) growth. The value of FWHM at 50 mTorr is 0.78°, which is comparable to the value (0.72°) measured on $SrRuO_3/LaAlO_3$ film.[18] The lowest value of FWHM indicates that the best

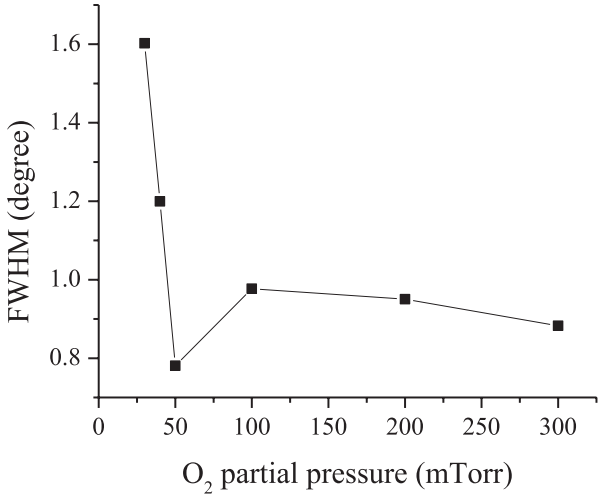


FIG. 3. Dependence of crystallinity of $SrRuO_3$ thin films on O_2 partial pressure. The value of FWHM is from the ω-rocking curve for the $SrRuO_3$ (002) reflection.

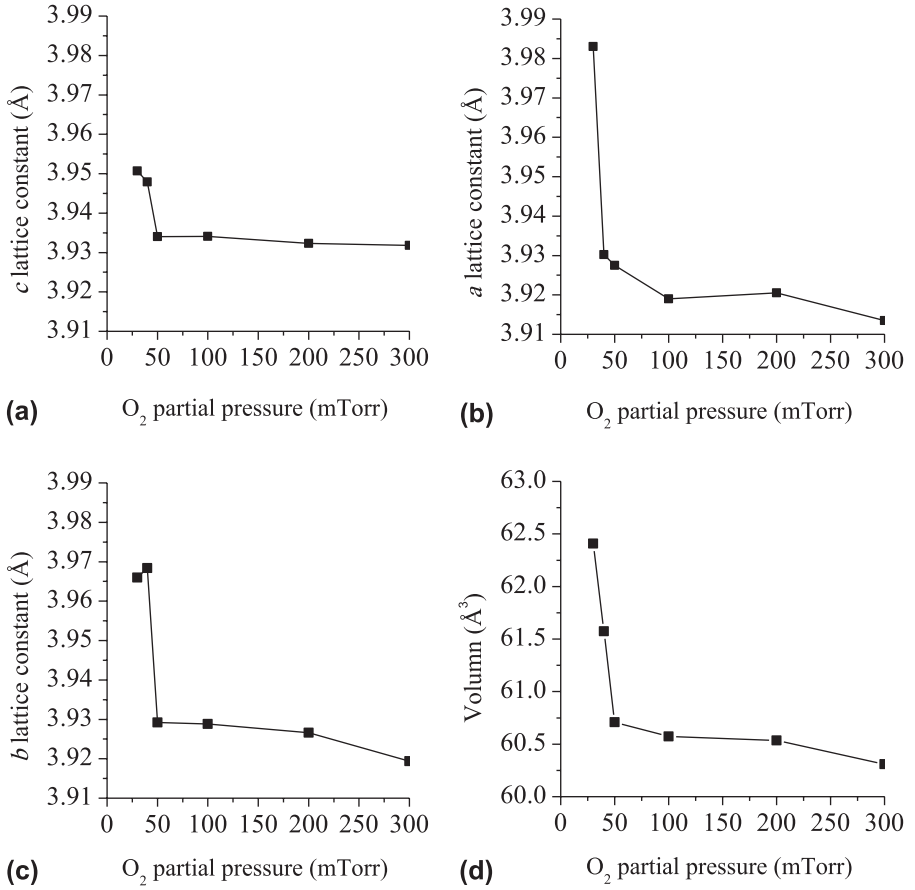


FIG. 4. (a) Out-of-plane lattice constants of $SrRuO_3$ thin films determined from the θ–2θ scans; (b) and (c) in-plane lattice constants determined from grazing incidence scans; and (d) volume of unit cell for $SrRuO_3$ thin films deposited at different O_2 partial pressures.

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crystallinity of $SrRuO_3$ thin film was obtained at 50 mTorr O_2 partial pressure.

$SrRuO_3$ (002) diffraction peaks shifted to higher 2θ angles as the working pressure was increased, indicating that the out-of-plane lattice constant was shortened in response to the increasing oxygen pressure. However, as the O_2 pressure further increases from 100 to 300 mTorr, an additional peak (112) became more distinguishable. Therefore, it was observed that film grown at 50 mTorr O_2 partial pressure was epitaxial (00*l*)-oriented single crystal.

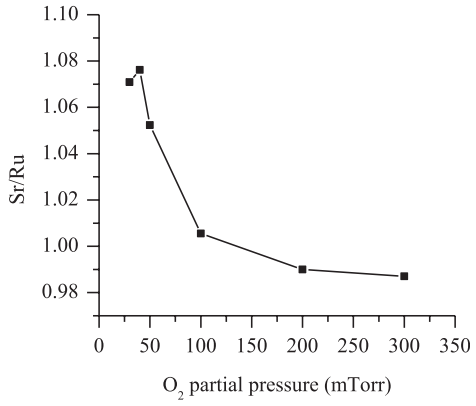


FIG. 5. Intensity ratio of Sr and Ru peaks measured from EDX profiles of $SrRuO_3$ films grown at different O_2 partial pressures.

The $SrRuO_3$ film deposited at 10 mTorr O_2 pressure has only one diffraction peak (i.e., the lattice constant evaluation error was not satisfactory), and therefore, this lattice constant was excluded from further consideration. The evaluated lattice constants for films grown at 30–300 mTorr O_2 partial pressure range are shown in Figs. 4(a)–4(c). To avoid ambiguity, all analyzed films had the same thickness of 150 nm. Films grown at the lower O_2 pressure (from 30 to 50 mTorr) had significantly larger out-of-plane lattice constants compared with that of the bulk $SrRuO_3$ (3.93 Å). This residual strain is mainly due to the lattice mismatch between film and substrate.

The phenomenon of out-of-plane lattice constant decreasing with the increase in the O_2 pressure is in good agreement with the result observed for the $SrRuO_3$ thin films deposited

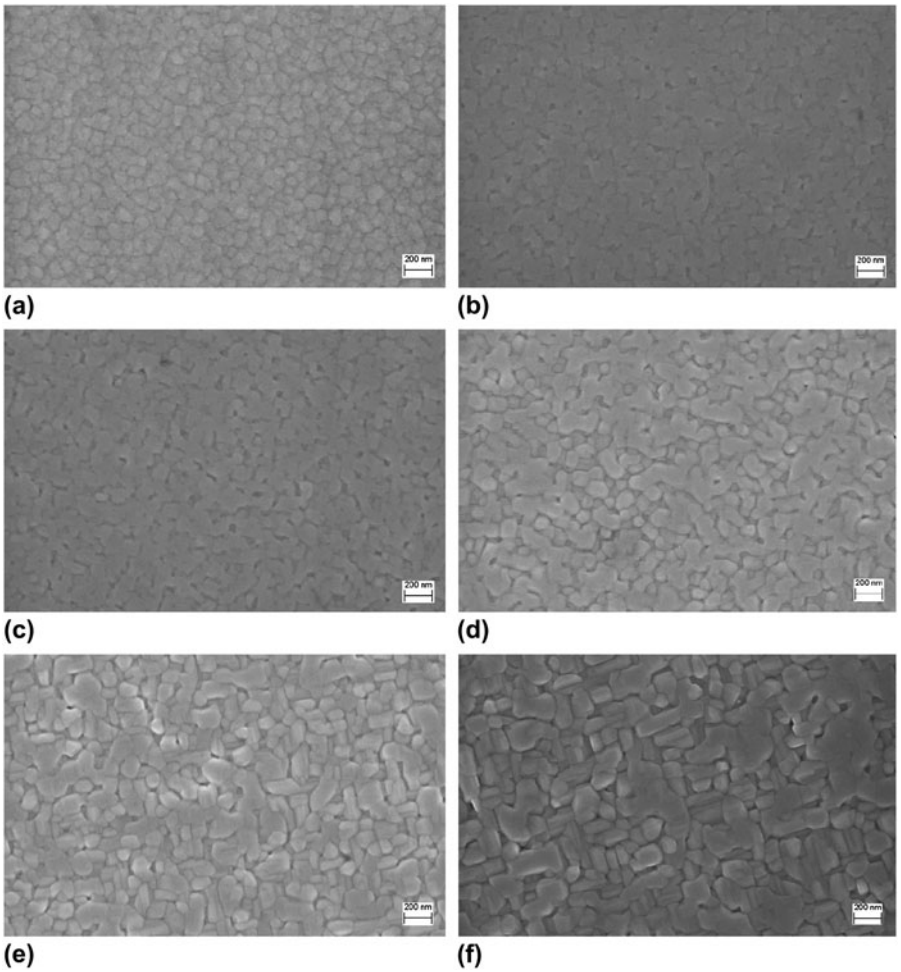


FIG. 6. SEM images of $SrRuO_3$ thin films grown at (a) 10 mTorr, (b) 30 mTorr, (c) 40 mTorr, (d) 100 mTorr, (e) 200 mTorr, and (f) 300 mTorr O_2 partial pressure. The magnification for (a)–(f) is 100,000x.

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on $SrTiO_3$ substrates.[8] The same phenomena were observed for the in-plane lattice constants too. The reason is that at low oxygen pressure, films are prone to lose Ru during the deposition. The Ru deficiency in the crystal structure causes crystal unit cell elongation in all the dimensions (i.e., increase of the unit cell volume) as shown in Fig. 4(d).

The Ru loss was further confirmed by the EDX measurement shown in Fig. 5. The analysis indicated that the films grown below 100 mTorr are Ru deficient, whereas the films grown above 100 mTorr exhibit a ratio of Sr and Ru close to one. This is a new result in comparison with the previously reported Ru deficiency in $SrRuO_3/SrTiO_3$ thin films deposited at O_2 partial pressures from 0.1 to 300 mTorr.[3]

Sample morphology was studied by SEM (Fig. 6) and showed that the grain size of the $SrRuO_3$ thin films increases when the deposition oxygen partial pressure increases. The SEM morphology of the $SrRuO_3$ film deposited at 300 mTorr displayed a larger grain size compared with the $SrRuO_3$ film deposited in 10 mTorr.

The resistivity of $SrRuO_3$ films was evaluated (at room temperature) using conventional four-point probe method. Figure 7 shows that a resistivity of $SrRuO_3/MgO$ thin films decreases with the increase of O_2 partial pressure. This can be explained by Ru loss at lower O_2 partial pressure. And also the larger grain size in films deposited at high O_2 partial pressure enhances electrical conductivity because of less grain boundary scattering of carries. A similar trend was observed on $SrRuO_3/SrTiO_3$ thin films, which showed higher resistivity of films deposited in a vacuum compared with films deposited at high O_2 pressure.[5] The $SrRuO_3$ films grown at 50 mTorr O_2 pressure showed a room temperature resistivity of 320 μΩ·cm.

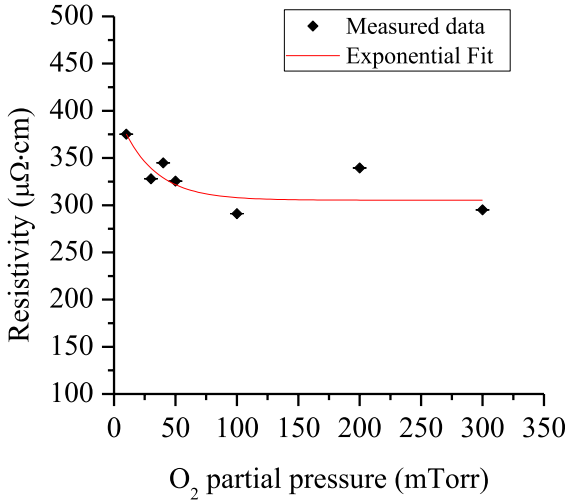


FIG. 7. Electrical resistivity as a function of O_2 partial pressure for $SrRuO_3$ thin films grown on MgO substrates.

IV. CONCLUSION

In summary, a comprehensive study of $SrRuO_3$ thin film growth on (001) MgO substrates by PLD in a wide oxygen pressure range from 10 to 300 mTorr was carried out. Crystalline $SrRuO_3$ films were obtained at the deposition temperature over 700 °C. However, at higher deposition temperature (>700 °C), an additional peak (112) was observed at 2θ of 57.3°. Appearance of this peak is reported for the first time (up to our knowledge, there are no previous reports of XRD studies of $SrRuO_3/MgO$ films performed above 2θ of 55°). The additional peak can be suppressed by reducing the O_2 partial pressure. The optimal deposition conditions of epitaxial $SrRuO_3$ thin films on MgO substrate were deposition temperature of 700 °C and 50 mTorr O_2 partial pressure.

Both the lattice constants and electrical resistivity of $SrRuO_3$ epitaxial thin films were found to depend on the growth oxygen partial pressure. The in-plane and out-of-plane lattice constants increased as the oxygen partial pressure was reduced. The results suggest that the elongated lattice constants for the films deposited at lower oxygen partial pressure were due to Ru loss during growth. The Ru deficiency in the crystal structure caused the unit cell to elongate in all dimensions (i.e., increase of the unit cell volume). The residual strain (due to the lattice mismatch between film and substrate) was also identified as contributing factor to the elongation of the lattice constants.

The oxygen pressure was found to have a direct effect on the resistivity of $SrRuO_3$ too. The resistivity of $SrRuO_3/MgO$ films decreases with an increase of the oxygen partial pressure.

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