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Keisuke Shibuya, Shaobo Mi, Chun-Lin Jia, Paul Meuffels, and Regina Dittmann

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Sr_2TiO_4 layered perovskite thin films grown by pulsed laser deposition

Keisuke Shibuya,[a] Shaobo Mi, Chun-Lin Jia, Paul Meuffels, and Regina Dittmann
Institut für Festkörperforschung, Forschungszentrum Jülich, D-52425 Jülich, Germany

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We have fabricated epitaxial Sr_2TiO_4 thin films on $SrTiO_3$ (100) single crystal substrates by pulsed laser deposition. We demonstrate that growth parameters including substrate temperature, oxygen pressure, as well as the laser fluence have to be chosen precisely to obtain stoichiometric well-ordered films of this complex layered structure. Films grown at low temperature showed three-dimensional random distribution of SrO double layers, causing a new extinction rule in x-ray diffraction. Stoichiometric Sr_2TiO_4 films with well-ordered SrO double layers were fabricated at higher temperature and under low oxygen pressures, where thermal energy was sufficient to compensate local composition fluctuation and Sr deficiency was very small. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2945640]

Thin film growth of layered perovskite oxides has attracted a great deal of attention in recent days because they are prototypes of high-temperature superconductors[1] and colossal magnetoresistance oxides,[2] which exhibit significant potential for applications. To develop comprehensive understanding on film growth of these materials will enable control over the crystal structure and allow them to be tailored for specific purposes.

Ruddlesden–Popper (RP) phases of $SrO-TiO_2$ system represented by the chemical formula $SrO(SrTiO_3)_n$ or $Sr_{n+1}Ti_nO_{3n+1}$ (n=integer) belong to a group of layered perovskite oxides with alternative stacking of perovskite $SrTiO_3$ layers and SrO rocksalt layers along the c axis.[3,4] The investigation of the thin film growth and the properties of this homologous series is highly necessary in the sense that the $n=\infty$ member, $SrTiO_3$, shows a variety of physical properties such as high Hall mobility at low temperature,[5] superconductivity,[6] large thermoelectric transport,[7] and ferroelectricity.[8,9] $SrTiO_3$ is, however, the only member of the series that melts congruently. Therefore single crystal of other members has been not reported.

Epitaxial growth of thin films under a thermodynamic nonequilibrium process such as molecular beam epitaxy (MBE) and pulsed laser deposition (PLD) could form metastable structures not generated in usual powder sintering. Epitaxial energy at the interface between the substrate and film is effective in stabilizing a specific crystal structure. Such techniques provide us possibilities to grow single crystal thin films of materials which do not melt congruently.[10] Nearly single phase $SrO(SrTiO_3)_n$ ($n=1-3$) have been deposited using MBE.[11] Nb-doped $SrO(SrTiO_3)_1$ films on $LaAlO_3$ (001) substrates have been recently reported to be fabricated by PLD.[12] On the other hand, initial attempts to prepare epitaxial $SrO(SrTiO_3)_n$ films on $SrTiO_3$ (001) using PLD were unsuccessful.[13,14] Very recently, another homologous series of Sr_nTiO_{n+2} ($n=1-5$) was grown by MBE.[15] Such crystal structure engineering is highly promising as it can create completely new materials that do not exist even as powder.

In this letter, we report thin film growth of Sr_2TiO_4 on $SrTiO_3$ (001) substrate by PLD. It has a lattice constant of $a=b=0.388$ nm and $c=1.260$ nm.[3] We paid close attention to growth parameters such as substrate temperature, oxygen pressure, and the laser fluence in order to obtain stoichiometric and high-crystalline films.

The thin films were fabricated on $5\times5\times0.5$ mm^3 $SrTiO_3$ (001) single crystal substrates (Shinkosha). The substrates were annealed at 1000 °C for 6 h in air to ensure flat surfaces. A KrF excimer laser operating at 1–2 Hz was used for ablation and the laser fluence was 0.5–3.5 J/cm^2 with a spot area of 5.0×1.1 mm^2. The target-substrate distance was set at 55 mm. The deposition was mainly performed under two different oxygen pressures of 3×10^{-4} and 0.25 mbar. Substrate temperatures were in the range from 600 to 900 °C. After fabrication, the films were cooled down to room temperature at 500 mbar of oxygen pressure. The growth rate per a laser shot was approximately 0.07 nm at 2.2 J/cm^2 of laser fluence, which was nearly independent of oxygen pressure below 0.25 mbar. It exhibited a linear relationship against the laser fluence with a threshold of around 0.4 J/cm^2. The thickness of Sr_2TiO_4 film was about 100 nm. The epitaxial growth of Sr_2TiO_4 films on $SrTiO_3$ (001) was confirmed by x-ray diffraction (XRD) using Cu $K\alpha$ radiation. Transmission electron microscopy (TEM) was used to investigate detail atomic arrangement of the films. Film composition was examined by secondary ion mass spectroscopy (SIMS). The analyzed area was 300 $\times$300 μm^2.

XRD results of the Sr_2TiO_4 films fabricated at temperatures from 700 to 900 °C are shown in Fig. 1. The oxygen pressure and the laser fluence were kept at 3×10^{-4} mbar and 2.2 J/cm^2, respectively. Only (006) and (00$\underline{12}$) peaks of Sr_2TiO_4 were detected in the film grown at 700 °C while all (00$\underline{2l}$) peaks (l=integer) were clearly observed in the highest-temperature film. The full width at half maximum of the omega rocking curves for the (006) peaks was about 0.05° for all films. A result similar to the sample deposited at 700 °C was reported by Salvador.[14] Their growth temperature was as low as 650 °C. In turn, all (00$\underline{2l}$) peaks were seen in films fabricated at 950 °C.[12] It seems that growth temperature is a main factor for the disappearance of (00$\underline{2l}$) ($l\neq3m$; m=integer) peaks in XRD.

TEM images of the films grown at 700 and 900 °C are presented in Figs. 2(a) and 2(b), respectively. Random distri-

[a]Author to whom correspondence should be addressed. Electronic mail: k.shibuya@fz-juelich.de.

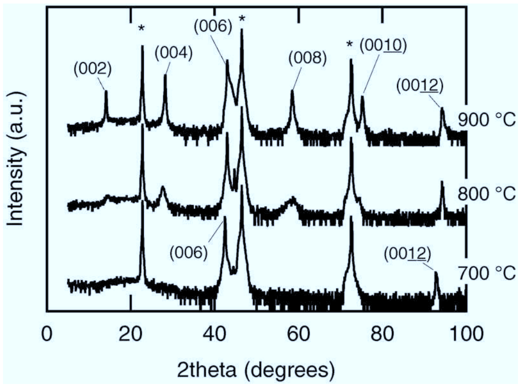

FIG. 1. XRD patterns of Sr_2TiO_4 films on $SrTiO_3$ (001) grown at different temperatures from 700 to 900 °C. Substrate peaks are labeled with *.

bution of SrO double layers both vertically and laterally can be seen in Fig. 2(a). Similar structures were observed in $Sr_5Ti_4O_{13}$ films grown by MBE (Ref. 16) and $(SrTiO_3)_5/(SrO)_1$ superlattices by PLD at low temperature.[13] Such vertical distribution of SrO double layer might be attributed to local substitution of Sr for Ti site to minimize interfacial energy in Sr-rich parts of the films[17] caused by regional composition fluctuation during film growth by PLD. Thermal energy to construct a local ordering of Sr_2TiO_4 was insufficient at such a low temperature, resulting in missing peaks in XRD because random distribution of SrO double layer creates a new extinction rule on a macroscopic scale. The structure factor along c axis of Sr_2TiO_4 is expressed as

$$F_{00l} = f_{\mathrm{Sr}} \exp(2\pi i l \omega_{\mathrm{Sr}}) + f_{\mathrm{Ti}} \exp(2\pi i l \omega_{\mathrm{Ti}}) + f_{\mathrm{O}} \exp(2\pi i l \omega_{\mathrm{O}}),$$

where l is the Miller index, ω_{Ti}, ω_{Sr} and ω_{O} are atomic positions in the unit cell, and f_{Sr}, f_{Ti}, and f_{O} are atomic scattering factors for Sr, Ti, and O, respectively. $(00l)$ peaks appear only when l is even because F_{00l} becomes zero in case l is odd.[3] Since Sr_2TiO_4 has an alternate stacking of TiO_2 and double SrO layers, there are three possibilities of local stacking along c axis: $TiO_2/SrO/SrO$, $SrO/TiO_2/SrO$, and $SrO/SrO/TiO_2$. When distribution of SrO double layer is random, translation vectors $[000]$, $[00\underline{1/3}]$, and $[00\underline{2/3}]$ must be included in the global structure factor. As the probabilities of those three structures are globally equal, the structure factor is modified as

$$F_{00l} = \frac{1}{3}\sum_{j=0}^{2} \{ f_{\mathrm{Sr}} \exp[2\pi i l(\omega_{\mathrm{Sr}} + \omega_j)] + f_{\mathrm{Ti}} \exp[2\pi i l(\omega_{\mathrm{Ti}} + \omega_j)] + f_{\mathrm{O}} \exp[2\pi i l(\omega_{\mathrm{O}} + \omega_j)] \},$$

where $\omega_0 = 0$, $\omega_1 = 1/3$, and $\omega_2 = 2/3$. F_{00l} is nonzero only for $l = 6m$ (m = integer). In the other cases, diffraction is out of phase globally. This is the reason why $(00\underline{2l})$ $(l \neq 3m)$ peaks were extinct in the XRD scan of low-temperature films.

On the contrary, one can observe a well-ordered structure in Fig. 2(b). This is consistent with the XRD result showing $(00\underline{2l})$ peaks of the films grown at 900 °C in Fig. 1. Larger thermal energy contributes to long-range migration of ablated species on the substrate, which compensates the local composition fluctuation. The surface migration length at 900 °C is estimated to be roughly one or two orders of magnitude larger than that at 700 °C. No RP defects in the lateral direction were seen in the sample. Sr_2TiO_4 films with ordered RP layer along c axis were fabricated at 900 °C and under low oxygen pressure.

Recently, correlation between the laser fluence and film composition was investigated in $SrTiO_3$ homoepitaxy.[18] The cationic ratio can be adjusted by the laser fluence. Lower (higher) laser fluence provides Sr (Ti) excess composition which results in an expansion of the lattice constant. A lattice constant variation affected by the laser fluence was also observed for the layered structure of Sr_2TiO_4 on $SrTiO_3$ (001). Figure 3(a) shows out-of-plane lattice constants against the laser fluence at two different temperatures of 700 and 900 °C. Two deposition oxygen pressures of 0.25 and 3×10^{-4} mbar were used at each temperature. X-ray reciprocal space mapping and electron diffraction indicated that in-plane lattice constants were completely restricted by that of the $SrTiO_3$ substrate. Therefore, the change of the out-of-plane parameters was caused not by strain effect from the substrate but by alteration of the unit-cell volume of Sr_2TiO_4. The lattice constant increased with lower laser fluence at a fixed temperature and under a constant oxygen pressure. On the other hand, higher laser fluence provided the diminishment of the lattice constant. These behaviors are consistent with the result for $SrTiO_3$ homoepitaxy when we assume that lower (higher) laser fluence provides Sr (Ti) excess films. Because the interlayer distance of a SrO double layer is estimated to be 0.2380 nm (Ref. 19) and that of SrO and TiO_2 layers is 0.1953 nm, the Sr (Ti) excess composition results in expanded (shrunk) lattice constant. In order to illustrate the observed behavior, average interlayer distances of strontium titanates are plotted as a function of Ti cationic ratio in Fig. 3(b). The values of $Sr_{n+1}Ti_nO_{3n+1}$ RP phases are from bulk[3,4] and those of Sr_nTiO_{n+2} are from thin films.[15] The indicated rectangle corresponds to the region of Fig. 3(a).

When deposition was performed at higher temperature and under higher oxygen pressure, the lattice constant became drastically smaller as shown in Fig. 3(a), indicating a Sr deficiency. Indeed, a SIMS analysis for a sample depos-

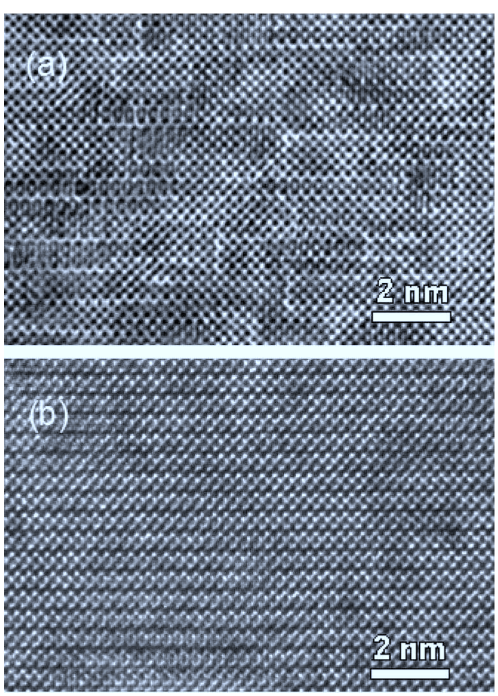

FIG. 2. TEM images of Sr_2TiO_4 films grown at (a) 700 °C and (b) 900 °C.

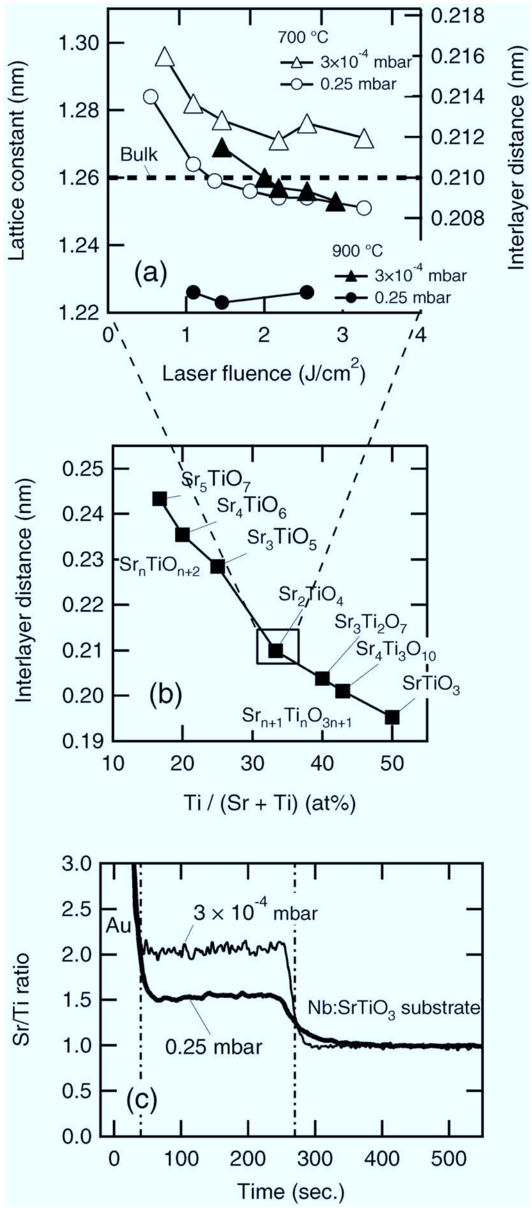

FIG. 3. (a) Out-of-plane lattice constant against the laser fluence at two different temperatures of 700 °C (open) and 900 °C (filled). The deposition was done at two typical oxygen pressures at each temperature. (b) Average interlayer distance of strontium titanates as a function of Ti cationic composition. (c) The Sr/Ti ratio depth profile of Sr_2TiO_4 films fabricated under oxygen pressures of 0.25 and 3×10^{-4} mbar.

ited at such conditions, 0.25 mbar and 900 °C, showed a Sr/Ti ratio of 1.5 while that for a film grown under an oxygen pressure of 3×10^{-4} mbar and at a temperature of 900 °C indicated almost stoichiometry, 2 as presented in Fig. 3(c). The laser fluence was set at 2.2 J/cm^2 in both cases. A 20-nm-thick gold layer was deposited on the surfaces to avoid a charging effect during the measurements. Here, 0.5 wt % Nb-doped $SrTiO_3$ substrates were used for the SIMS characterization and Sr/Ti ratio of the substrate was considered to be 1 as a standard. Higher oxygen pressure provided Sr deficiency at both 700 and 900 °C, and the degree of deficiency became larger at the higher temperature, implying a thermal effect on it. The nonstoichiometry was significant at pressures above 0.1 mbar. The Sr deficiency occurred under argon environment as well as under oxygen ambient, indicating that the Sr deficiency has a pressure dependence but is not due to a simple oxidation process. Sr-deficient films were also reported for $SrTiO_3$ under high oxygen pressures.[20] These results implied that SrO or Sr-related compounds sublimated during deposition under high pressure. However, the detailed mechanism will be clarified in the future.

In conclusion, high crystallinity thin films of a complex layered perovskite, Sr_2TiO_4, were epitaxially grown on $SrTiO_3$ (001) substrates by simple PLD method. Random distribution of SrO double layer was found in low-temperature grown films and a well-ordered structure was attained at higher temperature. Nearly perfect Sr_2TiO_4 films in terms of stoichiometry and microstructure were fabricated at substrate temperatures above 900 °C and under oxygen pressures below 0.1 mbar, where thermal energy was sufficient to construct well-ordered microstructure compensating local composition fluctuation and Sr deficiency was small enough to maintain stoichiometry.

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